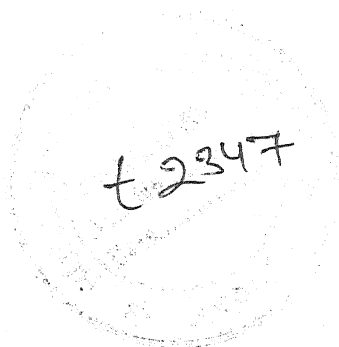# SYNTHESIS AND STUDIES ON SOME LEAD (II) COORDINATION COMPOUNDS

A
THESIS

Submitted to

Bundelkhand University, Jhansi

For the Award of the Degree of

DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

By

SHARAT SRIVASTAVA

POST GRADUATE DEPARTMENT OF CHEMISTRY
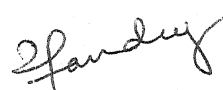## BIPIN BIHARI COLLEGE, JHANSI
INDIA
DEC. 2005

Dr.Yogesh Pandey
Reader in Chemistry
Bipin Bihari (P.G.) Science College
Jhansi

Date : 24/12/03

CERTIFICATE

Certified that the work embodied in this thesis entitled *"Synthesis and Studies on some Lead (II) coordination compounds"* is the result of original researches carried out by *Mr. Sharat Srivastava* under my supervision and is suitable for submission for the award of Ph.D. Degree of University of Bundelkhand Jhansi.

(Dr. Yogesh Pandey)

DECLARATION

I hereby declare that the thesis entitled *"Synthesis and Studies on some Lead (II) coordination compounds"* being submitted for the degree of Doctor of Philosophy to the Bundelkhand University (U.P.), is an inovative piece of work carried out with utmost dedication by me and to the best of my knowledge and belief it has not been submitted elsewhere.

(Sharat Srivastava)

Place : Jhansi

Dated : 24|12|05

ACKNOWLEDGEMENT

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In last but not least thanks are also due to my family members who have been a great source of inspiration patience and moral encouragment to me.

(Sharat Srivastava)

CONTENTS

CHAPTER - I

INTRODUCTION

The very easy extraction of lead from its ores made it one of the few metals used extensively from earliest times[1]. One of the earliest dated specimens is a lead statue found in the Dardanelles on the site of the ancient city of Abyodos. This is believed to date from 3000 B.C.

Lead was in common usage in Ancient Egypt for ornamental objects and solder, and lead salts were used to glaze pottery. The Hanging Gardens of Babylon were floored with sheet lead as a moisture retainer, and the Babylonaians and other ancients used lead for caulking and for the fastening of iron bolts and hooks in bridges, houses and other stone buildings.

The most extensive use of lead by the ancients was for the manufacture of water pipes. The Romans produced lead pipes in standard diameters and regular 10 ft lengths. Many such pieces of pipe work have been recovered perfectly preserved in modern times from ruins in Rome and many other Roman sites throughout Europe. Over four centuries, it is estimated, the Roman Empire extracted and used six to eight million tons of lead, with a peak annual production of around sixty thousand tons[2].

The most important ore of lead is galena or lead glance PbS, which is widely distributed throught the world[1]. Other are

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minerals of lead and anglesite ($PbSO_4$), Cerussite ($PbCO_3$), pyromorphite ($PbCl_2.3Pb_3(PO_4)_2$) and mimetesite ($PbCl_2.3Pb_3(AsO_4)_2$). Other lesser minerals are crocoite (or kallochrome, or red-lead ore) ($PbCrO_4$), Wulfenite (or molybdenum lead spar, or yellow lead ore) ($PbMoO_4$) and stolzite ($PbWO_4$).

The main sources of lead ores currently worked are in the U.S.A., Australia, Mexico, Canada and the U.S.S.R., but susbtantial quantities are mined in Peru, Morocco, Yugoslavia, Germany, Spain, South Africa, Italy and Bolivia.

Lead ores are initially crushed and concentrated by flotation, when lighter impurities such as zinc sulphide are removed. At this stage ore concentrates in general contain about 40% of lead by weight. The ore is roasted in air convert the sulphide to oxide and sulphate, in which process extensive evolution of sulphur dioxide takes place[4-20].

Lead may be further refined electrolytically upto 99.995%, and finally zone refining, produces lead better than 99.9999% pure[3].

In the earth's crust lead is estimated to be present as 1.6×10^{-3}% by weight, and to be in sea water at a concentration of 0.004 g/ton.

World production of lead is about two million tons a year,

2

but because lead is easily refined, and does not normally become contaminated in service, lead and lead-alloy scarp constitute an important factor in the lead market. it is estimated that over 80% of the lead used to manufacture batteries re-enters the market. The following list gives an approximate indication of some of the major consumers of lead : storage batteries (~35%), tetraethyl lead (~10%), cable covering (~10%), solder (~10%), red lead and litharge (~5%), building lead (~5%), caulking (~5%). Other lead uses ar white lead, bearing metal, ammunition, type metal and radiation shields.

All compunds of lead are toxic, and lead poisonning has been long known and exhaustively studied[21]. Nevertheless, lead poisoning still constitutes one of the most important industrial hazards[22].

Minute quantities of lead are ingested regularly by humans from contaminated food and drink, but such quantities are easily eliminated by normal body processes. Causes of harmful accumulations in this way are now very rare.

Serious lead intoxication is now most frequently encountered by inhalation of vapours or dusts of lead and lead compounds. Thus the processes of spraying or sanding lead paints are extremely hazardous without proper protection. The specified

maximum allowable atmospheric pollution is 0.15 mg of lead per cubic metre of air.
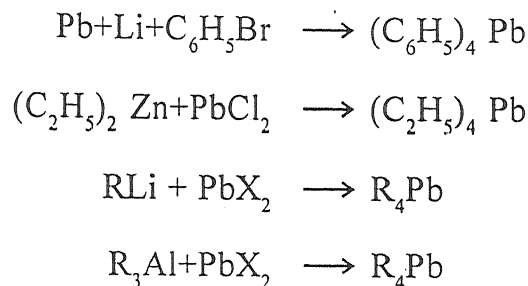
Lead poisoning can be cured and recovery is usually 100%. The most common treatment now is the intravenous injection of the sodium calcium salt of ethylenediaminetetra-acetic acid, which results in an immediate ten- to thirty-fold increase in the urinary excretion of lead. The clinical symptoms of lead poisoning are relieved in this way in a short time.

Tetraethyl-lead, together with tetramethyl-lead and the mixed ethylmethy-leads, is made on a larger scale commercially than all other organometallic compounds together.

This renders it a fairly cheap chemical at about $0.35 per pound. A quarter of a million is used annually in the U.S.A. alone as an antiknock agent in motor fuels[23-26].
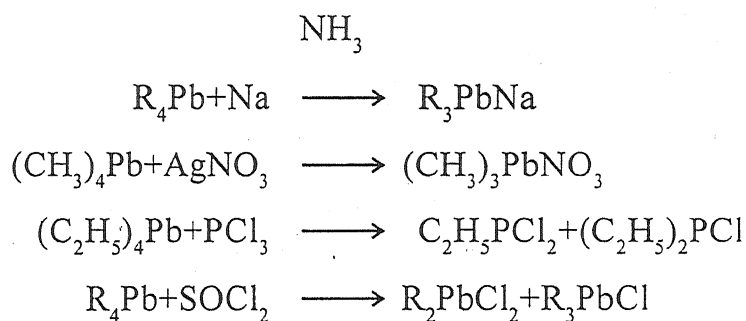
Industrially, the tetra-alkyl-leads are normally made by the action of alkylchoride sodium-lead alloy[26], or by the electrolysis of alkylmagnesium halides using a sacrificial anode, where the anode is attacked by alkyl radicals or anions. On a laboratory scale, ever, the action of a Grignard reagent upon lead (II) halide remains the favoured synthesis especially of the alkyl compounds R_4Pb[27]. In the case of aryl compounds, R_6Pb_2 is formed and has to be treated with halogen to produce R_3PbX, which is then further treated with

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Grignard to give R_4Pb[24]. Some other methods utilized to form lead (IV) carbon bonds outlined below.

$$Pb + Li + C_6H_5Br \longrightarrow (C_6H_5)_4 Pb$$

$$(C_2H_5)_2 Zn + PbCl_2 \longrightarrow (C_2H_5)_4 Pb$$

$$RLi + PbX_2 \longrightarrow R_4Pb$$

$$R_3Al + PbX_2 \longrightarrow R_4Pb$$

The lead (IV) alkyls and aryls are stable at ordinary temperatures, but release orgnic free radicals on heating Subsequent reactions are complex and among the pyrolysis products of tetramethyl-lead are 2-methyl-2-propene, propylene, ethylene, hydrogen, methane and ethane.

The fission of the lead-carbon bond is caused by a number of reagents as given below.

$$R_4Pb + Na \xrightarrow{NH_3} R_3PbNa$$

$$(CH_3)_4Pb + AgNO_3 \longrightarrow (CH_3)_3PbNO_3$$

$$(C_2H_5)_4Pb + PCl_3 \longrightarrow C_2H_5PCl_2 + (C_2H_5)_2PCl$$

$$R_4Pb + SOCl_2 \longrightarrow R_2PbCl_2 + R_3PbCl$$

From various studies the following series of relative ease of cleavage by halogen or halides has been established for organic groups attached to lead: α-naphthyl, *p*-xylyl, *p*-tolyl, phenyl, methyl, ethyl, *n*-propyl, isobutyl, isoamyl, cyclohexyl (least easily cleaved)[24].

The only well-defined examples of lead(II) organometallic compounds are bis(cyclopentadienyl) lead(II) and its ring methyl derivative. In the gas phase this has a bent sandwich structure as shown in Fig. 1 (a). Such a structure is also proposed to account for the solution spectra of $(C_5H_5)_2Pb$, where the two rings are believed bonded to two sp^2 lead hybrid orbitals, and a further sp^2 orbital contains a non-bonding pair of electrons. Such a bonding situation is in accord with the crystal structure of the orthorhombic form shown in Fig. 1 (b).
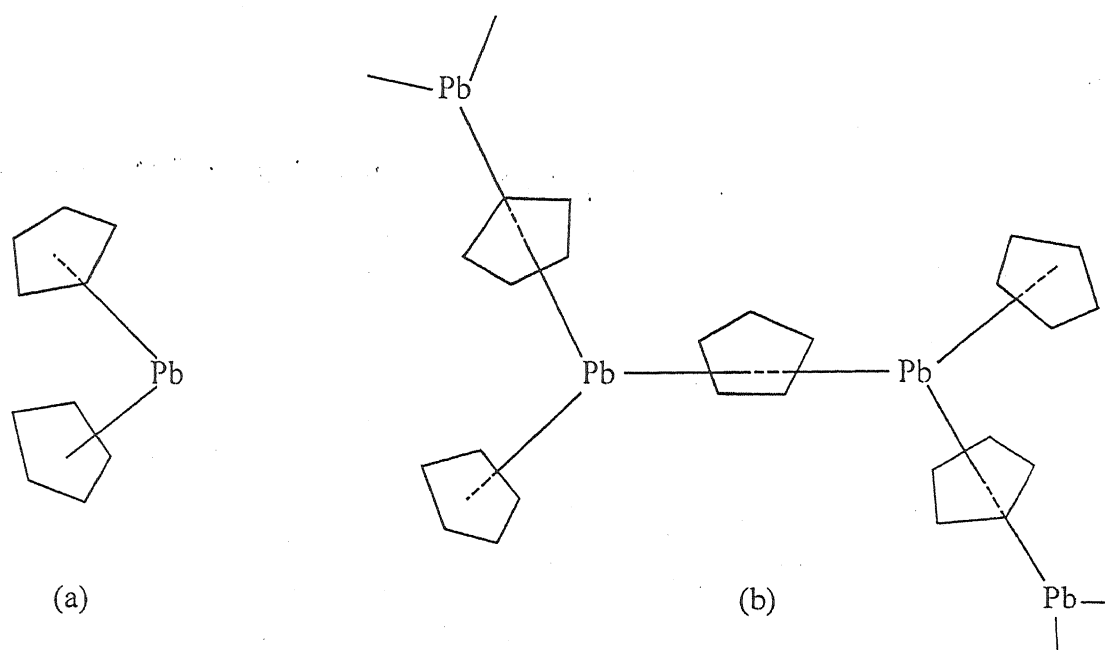

(a)   (b)

Fig.1. The structure of $(C_5H_5)Pb$: (a) in the gas and solution and (b) in the orthorhombic crystal for.

Here each lead atom is attached to two bridging cyclopentadienyl groups and one terminal cyclopentadienyl group[31]. The lead to ring

bonds are all at approximately 120°, and the polymer may be considered to arise by the lone pair of electrons on each monomer interacing with a cyclopentadienyl ring of another monomer.

A monoclinic from of $(C_5H_5)_2$ Pb is of unknown structure.

HYDRIDES

Lead hydride is the least well characterized of the Group IVB hydrides. It is formed along with hydrogen, on the electrolysis of dilute sulphuric acid with lead electrodes, and by the dissolution of lead-magnesium alloy in dilute acid[32]. The hydride of lead formed in small quantities is assumed to be PbH_4 (b.p.~-13°C)[33].

In alkali or weakly acid solutions, lead cathodes disintegrate at high current densities. This is believed due to the formation of the unstable hydribe PbH_2 at the cathode, and at current densities over 10-50mA/cm² the formation of PbH_2 was believed to be quantitative[34].

A lead hydride has been reported from the bombardment of lead films by hydrogen atoms[35].

Organolead Hydrides

The organohydrides of lead (IV) are not as robust as the corresponding compounds tin, germanium and silicon, but are nevertheless sufficiently stable for an extensive study the lead-hydrogen bond to be made.

Trialky-lead hydrides and dialkyl-lead dihydrides were made by reducing the corrsponding chlorides with lithium alluminimum hydride at low temperature (-78^0)[36,37,38].

The exchange reaction between organotin hydrides and organolead salts has also prove a useful synthesis for organolead salts has also prove a useful synthesis for organolead hydrides[39].

$$(n-C_4H_9)_3\ PbX+(C_6H_5)_3SnH \longrightarrow (n-C_4H_9)_3PbH+(C_6H_5)_3SnX$$
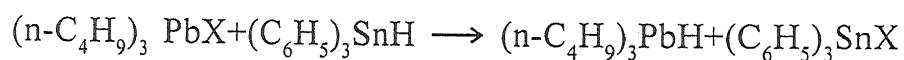
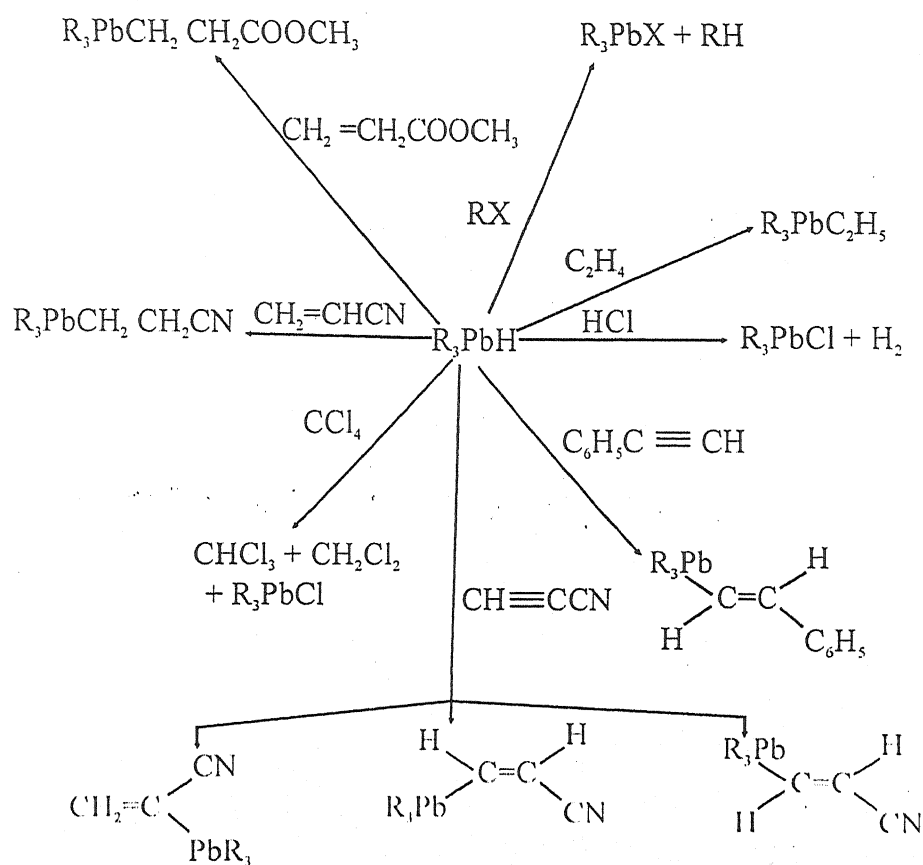Trimethyl-lead hydride (m.p. ~ - 106^0) and triethyl-lead

Fig.2.Some reactions of the lead-hydrogen bond in trialkyl-lead hydrides.

hydride (m.p. ~ 145 were found to decompose to the corresponding tetra-alkyl-lead, lead metal and hydrogen. Evolution of hydrogen begins on warming to about -30^0 to -20^0, but even at 0^0 the hydrides are not completely decomposed for several hours.

Some of the reactions of trialky-lead hydride are outlined[40] in Fig.2.

Very unstable trialky-lead borohydrides have been made from organolead alkoxides and diborane at -78^0.

$$4R_3PbOCH_3 + 3(BH_3)_2 \longrightarrow 4R_3PbBH_4 + 2HB(OCH_3)_2$$
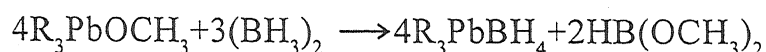
These trialky-lead borohydrides react with methanol to release trialkyl-lead hydrides, and decompose at about-30^0 to hexa-alkyldileads[41].

COMPOUNDS OF NITROGEN, PHOSPHORUS ARSENIC, ANTIMONY AND BISMUTH

(a) *Binary Compounds*

Lead(II) azide is discussed with the pseudohalides, and lead nitrides are not known.

The phosphides of lead are not well characterized and appear to interconvert easily[42]. PbP_5 was obtained from a liquid ammonia solution of rubidium phosphide and lead nitrate. PbP_5 is

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spontaneously inflammable in air, and dissociates on heating with loss of phosphorus[43].

The action of phosphine upon alcoholic lead acetate solution produces Pb_3P_2[44].

Arsine and lead(Il) acetate form the very unstable arsenide Pb_3As_2[45].

In addition to these few binary compounds of lead with the Group VB elements, there is a considerable range of mineral compounds which contain lead, and either arsenic, antimony or bismuth, but these are ternary and quaternary materials such as sartorite $PbAs_2S_4$ dufrenoysite $Pb_2As_2S_5$, sperrylite $Pb_4As_2S_7$, sakharovite $PbBiSbS_4$ and semseyite $Pb_9Sb_8S_2$.

(b)   Organolead Amines, Phosphines, Arsines and Stibines

In addition to the binary compounds there are a few examples of discrete lead-nitrogen[46], lead-phosphorus, lead-arsenic and lead-artimony bonds in various compounds, but they are considerably more rare than the corresponding compounds of tin, germanium and silicon.

Coordination compounds such as the di-ammine of diphenyl-lead dibromide contain discrete lead-nitrogen bonds, but such complexes are very unstable[47]. In the case of the diaryl-lead

oxinates, however, the coordinate nitrogen-lead bond is quite stable[48].

The first organolead amine reported[49] was sec-$C_4H_9.NH.Pb(C_2H_5)_3$, prepared from triethyl-lead chloride and sodium sec-butylamide. Other amines of lead include $(CH_3)_3PbN(CH_3)Ge(CH_3)_3$[50] and $(CH_3)_3PbN[Si(CH_3)_3]_2$[51].

In addition to these ammines, many organolead sulphonamides, phthalimides and sulphimides contain lead—nitrogen bonds[52,53,54]. The sulphimides, phthalimides and sulphonamides are not hydrolysed by water, in marked contrast to the organolead amines.

The mono-, bi- and tri-lead phosphines exemplified by $(C_6H_5)_3PbP(C_6H_5)_2$[55], $[(C_6H_5)_3P]_2PC_6H_5$[56] and $[(C_6H_5)_3Pb]_3P$[57] are all crystalline solids which decompose readily upon warming. They are synthesized by the reaction of organolead halides with the requisite phosphine. The same method, along with the metathetical removal of sodium chloride from the organolead halide and the requisite sodium arsenide or stibnide, is used to prepare the organolead arsines and stibines.

OXYGEN COMPOUNDS

(a) Oxides of Lead

Lead(II) oxide (litharge) is the oxide of lead formed when lead is heated in the air. The industrial preparation involves blowing air into molten lead.

Two crystal forms of lead(II) oxide are known: the yellow orthorhombic form is the stable form above 488^0C, and the red tetragonal form is stable at ordinary temperatures[58].

Ultrapure PbO is made by precipitation from lead acetate solution by ammonium hydroxid in polyethylene vessels. In such wet preparations of lead(II) oxide, the yellow orthorhombic form is first produced which undergoes transformation to the red tetragonal PbO. This transformation is particularly sensitive to impurities, and the presence of elements such as silicon, germanium, phosphorus, arsenic, antimony, selenium, tellurium, molybdenum and tungsten in concentrations as low as 10 ppm prevents the transformation. The use of polythene vessels for the preparation of ultrapure red lead(II) oxide is emphasized, because sufficient silica is released from glass vessels to prevent the yellow to red conversion[58,59].

The so-called "black" lead(II) oxide is merely yellow or red PbO with a thin surface film of elemental lead.

In tetragonal lead(II) oxide[a], each lead atom has four oxygen near neighbours, all lying to one side, and all of the oxygen atoms lie between every other pair of lead layers as in Fig. 3.

The oxygen atoms in rhombohedral PbO have proved impossible to locate by X-ray intensity measurements[61], but their positions were determined by neutron diffraction[62]. The structure consists of a chain in which lead has two nearest oxygen neighbours (Pb-O = 2.21Å). These chains are loosely bonded into layers by two Pb-O bonds (Pb-O= 2.49 Å).

The layer in rhombohedral PbO is a slightly puckered version of that in tetragonal PbO_2 where four equal Pb-O bonds (2.30 Å) replace the two short (2.21Å) and two long (2.49 Å) Pb-O bonds. This close similarity of structures presumably allows small impurities to stabilize the yellow rhombic form at ordinary temperatures. The two crystal forms can be obtained simultaneously by heating lead carbonate at 400o in a melt of potassium and sodium nitrates, when over a period of one day red prisms of tetragonal PbO and yellow plates of rhombic PbO are formed along with orange needles of Pb_3O_4.
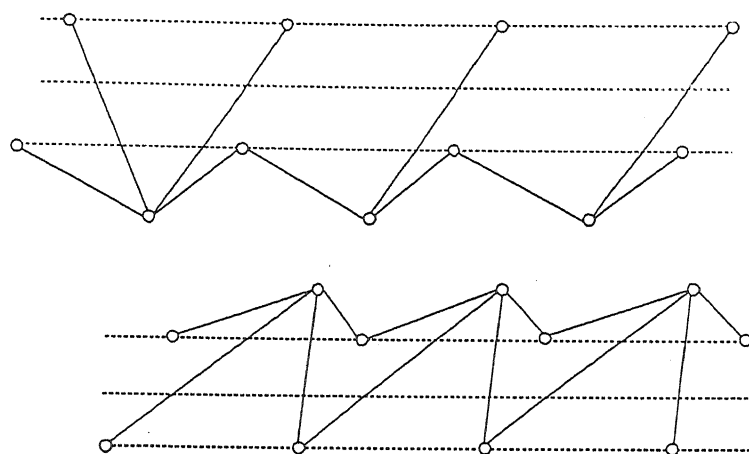
Fig.3. Tetragonal lead(II) oxide

Lead(IV) oxide can be obtained in a very pure form by the hydrolysis of lead tetraacetate[63,64]. In this form it is particularly reactive and useful as an oxidizing agent in organic chemistry. More usually lead (IV)) oxide is made by the hypochlorite oxidation of lead(II) acetate solutions[65], or by the action of nitric acid upon Pb_3O_4.

Formed in this way PbO_2 has the rutile structure, but another- orthorhombic form of PbO_2 is known[66]. This is prepared by the anodic deposition during electrolysis of lead acetate, lead nitrate or sodium plumbite solutions under specific conditions. This so-called α-form of PbO_2 has the niobite (columbite) type of structure, which consists essentially of a hexagonal close-packed assemblage of oxygen atoms in which one-half of the octahedral holes are occupied by Pb^{4+} ions. This gives the Pb^{4+} ion six oxygen nearest neighbours, two at 2.16 Å, two at 2.17 Å and two at 2.22 Å[66].
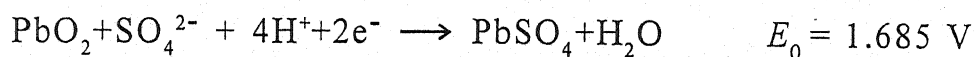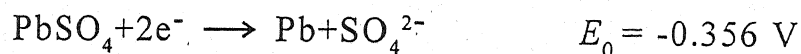
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Lead(IV) oxide is formed in nature as the somewhat rare mineral plattnerite, which is isomorphous with rutile and many other dioxides like SnO_2, MnO_2, ZrO_2 and ThO_2.

Lead (IV) oxide is difficult to obtain in a perfectly anhydrous state, as the temperature for complete drying initiates release of oxygen to form PbO and Pb_3O_4. If carefully heated in a stream of oxygen, however, completely anhydrous lead(IV) oxide can be made.

The action of heat decomposes lead(IV) oxide to oxygen (partial pressure of O_2 reaches one atmosphere at $344^{\circ}C$ with a coarse-grained PbO_2) and to Pb and Pb_3O_4. Lead(IV) oxide is a powerful reducing agent but is not a peroxide. Rapid grinding with sulphur or red phosphorus produces inflammation, explaining the use of lead(IV) oxide in matches.

Lead (IV) oxide is an essential constituent of the lead-acid accumulator. A single cell of the battery consists of one electrode of lead sponge and the other of a mesh of lead which is impregnated with lead (IV) oxide. The electrolyte is strong sulphuric acid.

The two electrode reactions are :

$$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-} \qquad E_0 = -0.356 \text{ V}$$

$$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + H_2O \qquad E_0 = 1.685 \text{ V}$$

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Acting in opposition the electrode reactions provide an overall potential of 2.041 V, but the potential delivered by the cell will depend upon temperature, the acid concentration and current flow.
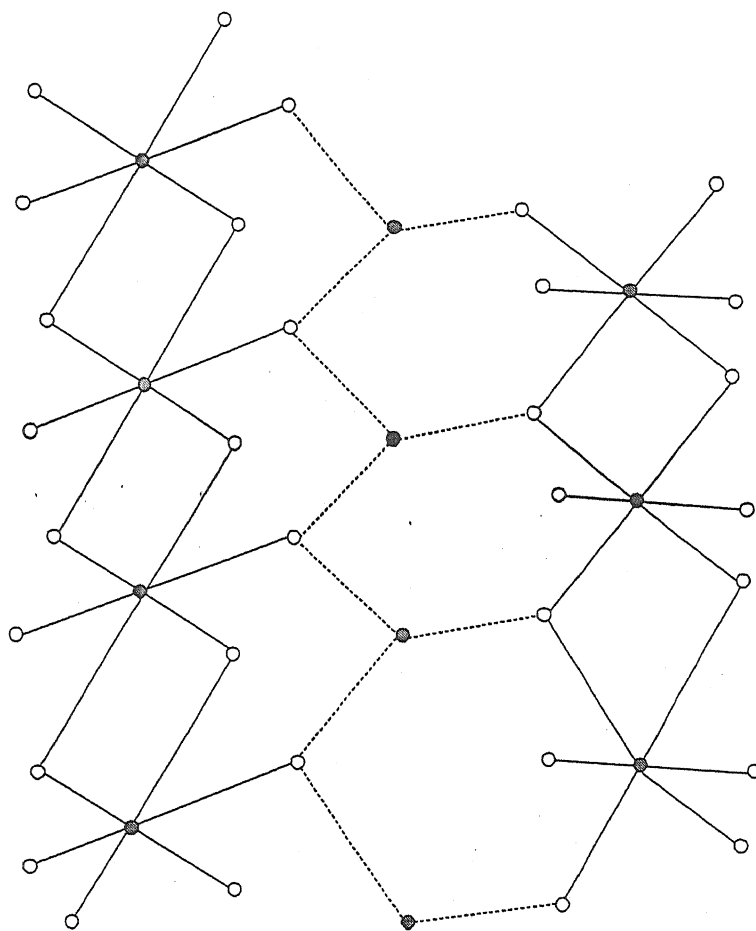

Fig.4. Structure of Pb_3O_4

Pb_3O_4 has a structure[67,68,69] which consists of chains of $Pb^{IV}O^6$. opposite edges; the chains are linked by Pb(II) ions

coordinated by pyramidally as in Fig. 4. Thus Pb_3O_4 can be looked upon as lead(II) plumbate, and nitric acid attacks Pb_3O_4 to, in effect, remove $2PbO$ and leave PbO_2.

The finely divided Pb_3O_4 (minium or red lead) used as a preservative and in paints is usually made by the action of heat upon PbO or $PbCO_3$ in a current of air. A macrocrystal line form is obtained by the slow crystallization of Pb_3O_4 from a mixed solution of $K_2Pb(OH)_4$ and $K_2Pb(OH)_6$[70], or alternatively from PbO_2 and sodium hydroxide in the presence of water in a steel bomb at about 375^0[71].

Pb_3O_4 evolves oxygen on heating, and the oxygen reaches a pressure of about 0.2 atm at about 550^0. If, however, dissociation into oxygen and lead(II) oxide is prevented by raising the oxygen pressure over Pb_3O_4, it melts at about 830^0.

Much has been written of oxides of lead, other than Pb_3O_4, which lie between compositions of PbO and PbO_2.

The differential thermal analysis of the decomposition of PbO_2, together with X-ray analysis, has shown two further oxide phases as illustrated below[72].

$$PbO_2 \xrightarrow{\text{about } 280^0} \alpha\text{-}PbO_z \quad (x \sim 1.66)$$

$$\alpha\text{-}PbO_z \xrightarrow{\text{about } 375^0} \beta\text{-}PbO_Y \quad (y \sim 1.5)$$

$$\beta\text{-}PbO_Y \xrightarrow{\text{about } 375^0} Pb_3O_4$$
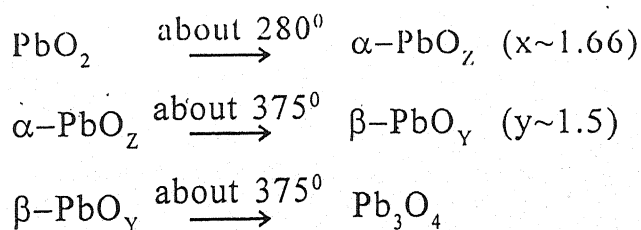
A monoclinic structure is proposed for $\alpha-Pb_7O_{11}$ Pb_5O_8 of earlier workers. $\beta-PbO_{1.5}$ has an orthorhombic structure, with composition Pb.

(b) Hydroxy Compounds :

There appears to be only one crystalline lead oxide-hydroxide, which has been formula as $3PbO.H_2O$[73]. Comparisons of the X-ray data with the corresponding tin compounds suggest that this compound is better written as $Pb_6O_8H_4$, with a structure shown in Fig.5 in which an octahedral Pb_6 cluster is contained in a cude of oxygen atoms, with hydroglen bonds between all oxygen atoms[74].
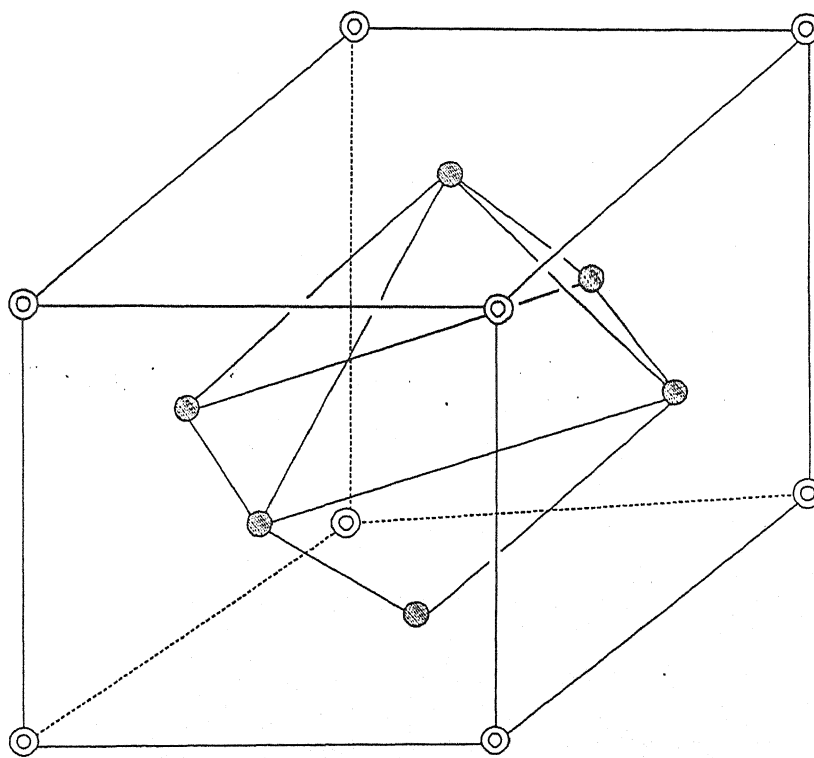
Fig.5. Proposed cluster structure of the Pb_6O_8 units in lead oxide-hydroxide. ⊕ =Pb; ◎ =O.

$Pb_6O_8H_4$ is obtained either by hydrolysis of lead(II) acetate solutions[75], or from reduce pressure evaporation of solutions of tetragonal PbO in large volumes of carbon dioxide from water[76]. Such a preparation and the proposed structure are in line with the hydroxy-lead(II) anions $Pb_3(OH)_4^{2+}$ and $Pb_3(OH)_6^{2+}$ which are reported in partially hydrolysed solutions of lead (II) salts. Such ions are likely to contain metal clusters.

When aqueous sodium hydroxide is added to a solution of lead nitrate, two basic nitrares are precipitated with stoichiometries $Pb(NO_3)_2.Pb(OH)_2$ and $Pb(NO_3)_2. 5Pb(OH)_2$. Even pH = 12 (which is considerably past the equivalence point), there is no indication of precipitation of $Pb(OH)_2$ as such[77].

Many other alkali precipitations from solutions of lead(II) salts have various basic salt formulations, and are often well-characterized crystalline materials.

If a current of air is passed through a solution of lead(II) acetate during the addition of sodium hydroxide solution, the carbon dioxide content of the air is sufficient to precipitate all of the lead as hexagonal platelets with the formulation $3PbCO_3. 2Pb(OH)_2$[78]. Another better-known basic carbonate of lead $2PbCO_3. Pb(OH)_2$ is formed when lead sulhate or lead chloride is boiled with sodium carbonate solution.

The Commercial product "white-lead" is of variable compositiion, but is essentially the $3PbCO_3 . 2Pb(OH)_2$ mentioned above. It is made by number of processes, which give different physical characteristics such as particle size, which affect it use as a white paint pigment.

In the Dutch and German "dry" processes lead sheet is exposed to acetic acid vapour and carbon dioxide. Lead acetate, basic lead acetate and finally basic lead corbonate (white lead) appear to be formed sequentially. The so-called French, English and Hebrew "wet" processes involve the formation of a suspension or dough of basic lead acetate by dissolving lead(II) oxide in boiling lead acetate solution. The subsequent passage of carbon dioxide produces the basic lead carbonate. The formation of black lead sulphide in sulphur-con- taining atmospheres is a drawback in the use of $2PbCO_3 . Pb(OH)_2$ as a white pigment.

$2PbCO_3 . Pb(OH)_2$ is found as a mineral hydrocerussite (or plumbonacrite) in many parts of the world, and has also been obtained as a corrosion product of lead roofing[79].

The complex formation between Pb^{2+} and OH^- has been studied in perchlorate solutions and the following complex ions are noted[80,81] to be present in solution before precipitation commences, $Pb(OH)_3^-$, $Pb_4(OH)_4^{4+}$, Pb_2OH^{3+}, $Pb_3(OH)_4^{2+}$, $PbOH^+$, $Pb_6(OH)_8^{4+}$, together with dissolved $Pb(OH)_2$.

The predominant ion present is $Pb_4(OH)_4^{4+}$, which is likely to have a cyclic bridged structure similar to that of $Sn_4(OH)_4^{4+}$.

The so-called metaplumbates $M^I_2PbO_3 \cdot 3H_2O$ are made by fusing lead(IV) oxide with an excess of potassium hydroxide[82,83]. These compounds are actually the alkali metal salts of the hexahydroxylead (IV) anion $Pb(OH)_6^{2-}$. The salts contain discrete $Pb(OH)_6^{2-}$ ions analogous to the corresponding $Pn(OH)_6^{2-}$, of tin(IV)[84,85]. $Na_2Pb(OH)_6$ has also been made by the electrolytic oxidation of alkali hydroxide solutions of Pb(II) and also by the controlled alkali hydrolysis of lead(IV) acetate.

(c) Plumbites and Plumbates :

Alkaline solutions of lead contain a complex set of lead hydroxo cations; but at low lead concentrations the anion $Pb(OH)_2$ present. This trihydroxyplumbite is also believed present when precipitated amphotericin "hydroxide" is dissolved in alkali. No evidence for the $Pb(OH)_4^{2-}$ anion has been found though solutions of lead "hydroxide" in strong potassium hydroxide solution are of written as $K_2Pb(OH)_4$.

There are two other types of plumbate. The alkali metal plumbates have the formulation $M^I_2PbO_3$. These are made by carefully controlled dehydration of the $M^I_2Pb(OII)_6$ of the alkali metals[86,87]. If the dehydration is not carefully controlled below 110^0,

however the $M_2^IPb(OH)_6$ decomposes with evolution of oxygen as well as water. Alternatively K_2PbO_3 along with $K_2Pb_3O_7$ can be made in a melt of KOH and PbO_2, and they are bonded isostructural with the corresponding stannates[88].

The metaplumbates of strontium and barium $M^{II}PbO_3$ are made by fusion of strontium or barium nitrates with lead (II) oxides. The oxides of nitrogen released convert into lead(II) to lead(IV). Calcium orthoplumbate Ca_2PbO_4 is formed when calcium nitrate along lead(II) oxide are fused in the stoichiometry $Ca(NO_3)_2.PbO$. The barium and stronitium orthoplumbates are prepared by heating barium or strontium carbonates with lead(II) oxide in the stoichiometry $(MCO_3)_2.PbO$; the necessary oxidation is caused by the atmosphere[90].

$BaPbO_3$ (density 8.30) has the ideal perovskite structure and $SrPbO_3$ (density 7.79) has some what deformed orthorhombic perovskite structure[91].

$BaPbO_4$ (density 7.34) is tetragonal with Pb-O distances 2.15 and 2.07Å and distance 2.66 and 2.88Å[89].

Neither the metaplumbates nor the orthoplumbates can be regarded as containing discrete PbO_3^{2-} and PbO_4^{4-} ions respectively[90].

(d) Oxy and Hydroxy Halides :

The lead oxyhalides Pb_2OCl_2, $Pb_3O_2Cl_2$ and Pb_3OCl_4 occure in nature reswpectively matlockite $(PbCl_2.PbO)$, mendipite $(PbCl_2.2PbO)$ and penfieldite $(2PbCl_2.PbO)$.

Lead oxyfluorides of unknown composition are reported from the passage of fluorination over PbO_2, or steam over PbF_2. An oxyfluoride Pb_2OF_2 is reported to be tetragonal[92].

In addition to the oxychlorides occurring as minerals, the two compounds Pb_2OCl_2 and $Pb_3O_2Cl_2$ can be made in a number of ways, including the action of the requisite amount of alkali upon lead chloride solutions. $Pb_3O_2Cl_2$ melts without decomposition at 693^0C, and the heat of formation from $PbCl_2$ and $2PbO$ is 9.24 kcal/ mole[93].

The compositions Pb_2OBr_2, $Pb_3O_2Br_2$ and $Pb_5O_4Br_2$ have been reported for the lead oxybromides, but only Pb_2OI_2 for the oxyiodides[93].

The chlorite, chlorate and perchlorate together with the corresponding bromine and iodine compounds are known with various formulae $Pb_xO_yX_z$, but these are discussed below as oxy-salts, and should not be confused with the lead oxyhalides.

The lead(II) hydroxychloride Pb(OH)Cl occurs as the

mineral laurionite, whose structure is closely related to that of lead(II) chloride. In Pb(OH)Cl lead exhibits nine coordination, with five chlorine atoms (Pb-Cl= 3.23 Å) and one hydroxide group (Pb-OH = 2.67Å) at the apices of a trigonal prism, and three further hydroxide groups in the quatorial plane beyond the centres of the prism faces[94].

An iodo-laurionite Pb(OH)I is made from a solution of lead acetate and warm lead iodide solution.

The lead(IV) oxychloride $PbOCl_2$ is prepared by the action of Cl_2O on a solution of lead(IV) chloride in carbon tetrachloride. $PbOCl_2$ (d.5.04 g/cc) is pale violet when completely dry, and appears to be amorphous. It decomposes at 95^0 to lead(II) chloride and oxygen, and is very hygroscopic, undergoing hydrolysis to lead (IV) oxide and hydrogen chloride[95].

(e)   Organolead Oxides, Hydroxides and Alkoxides :

The organolead hydroxides $R_2Pb(OH)_2$ and R_3PbOH are prepared by the alkaline hydrolysis of the corresponding halides. The correspoinding oxides $R_3PbOPbR_3$ and $(R_2PbO)_n$ are prepared by the action of sodium upon the hydroxides. The oxides are extremely sensitive to water, undergoing rehydrolysis to the corresponding hydroxides[96,97,98].

The trialky-lead hydroxides and oxides are not easy to

obtain completely pure, due to a marked tendency to decompose at room temperature. The triaryl-lead hydroxides, however are much more stable[99].

The solvated $(CH_3)_2Pb^{2+}$ ion has been studied in aqueous solution, and it is concluded that in the $[(CH_3)_2Pb(H_2O)_n]^{2+}$ complex, the $CH_3-Pb-CH_3$ skeleton is linear. The equilibria outlined below are for the hydrated $(CH_3)_2Pb^{2+}$ cation under various conditions of acidity[100].

$$(CH_3)_2Pb^{2+} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \left[(CH_3)_2Pb \begin{matrix} OH \\ \diagup \diagdown \\ OH \end{matrix} Pb(CH_3)_2 \right]^{2+}$$

pH < 5   pH 5-8

$$OH^- \downarrow \uparrow H^+$$

$$[(CH_3)_2Pb(OH)_3]^- \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} (CH_3)_2Pb(OH)_2^-$$

pH < 10   pH 8-10
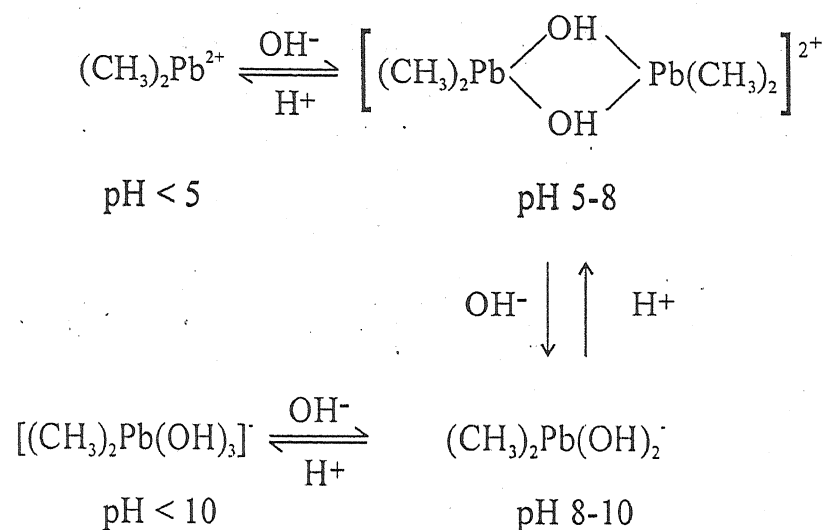
The ozonization of tetra-ethyl-lead at -68^0 gives an unidentified product which decomposes at room temperature to produce $(C_2H_5)_3PbOH$, $[(C_2H_5)_3PbO]_n$, $(C_2H_5)_3PbOC_2$ together with acetaldehyde and ethanol[101]. Good yields of the oxides $R_3PbOPbR_3$ obtained by the action of ozone upon the hexa-organodileads R_3PbPbR_3.

With alcohols some alkyl-leads undergo fission.

$$R_4Pb + R'OH \longrightarrow R_3PbOR' + RH$$
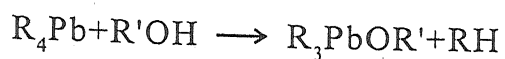
The alcohol reactivity falls off steadily from $R'OH = CH_3OH$ to $R'OH = C_4H_9OH$, when is unreactive[102].

The best preparation of organolead alkoxides involves the metathesis between sodium alkoxides and the organolead halides[103].

Trimethy-lead methoxide $(CH_3)_3PbOCH_3$ is polymeric, properties of the lead-oxygen bond in the organolead alkoxides and the organolead alkoxides and the organolead oxide have been investigated and many reactions of the "insertion" type are known, as shown by the equations below.

$$(C_6H_5)_3PbOCH_3 + CS_2 \longrightarrow (C_6H_5)_3Pb\text{-}S\text{-}\overset{\parallel}{\underset{S}{C}}\text{-}OCH_3$$

$$(C_4H_9)_3PbOCH_3 + Cl_3CCHO \longrightarrow (C_4H_9)_3PbO\text{-}\underset{CCl_3}{\overset{|}{C}H}\text{-}OCH_3$$

$$(C_6H_5)_3PbOPb(C_6H_5)_3 + Cl_3CCHO \longrightarrow (C_6H_5)_3PbO\underset{CCl_3}{\overset{|}{C}H}OPb(C_6H_5)_3$$

$$(C_6H_5)_3PbOCH_3 + C_6H_5NCS \longrightarrow (C_6H_5)_3Pb\text{-}S\text{-}\overset{\parallel}{\underset{N\text{-}C_6H_5}{C}}\text{-}O\text{-}CH_3$$

$$(C_6H_5)_3PbOCH_3 + (CCl_3)_2CO \longrightarrow (C_6H_5)_3PbO\underset{CCl_3}{\overset{\overset{CCl_3}{|}}{C}}OCH_3$$
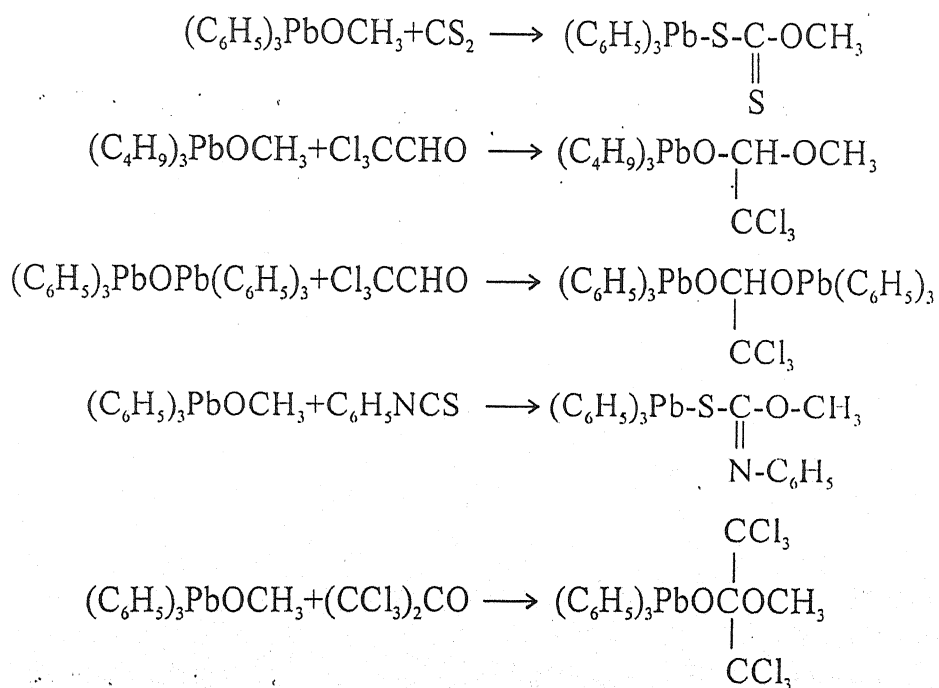
Many of the complexes of lead such as lead(II) oxinate which are used in lead analy presumably contain a lead-phenoxide type of linkage, but no structural data are available.

Triphenyl-lead 8-oxyquinolinate is reported to have four-coordinate in ethan but five coordinate in benzene solution Fig.6(a) and (b)[105]. In monophenyl tris (8-oxyquinolinate) only one of the nitrogen atoms can be quaternized by methyl iodide, suggesting the structure in Fig.6(c) in which lead is six-coordinate[106].
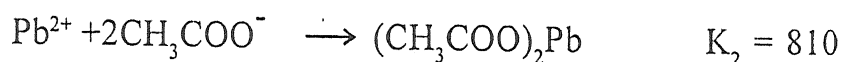

(a)

(b)

(c)
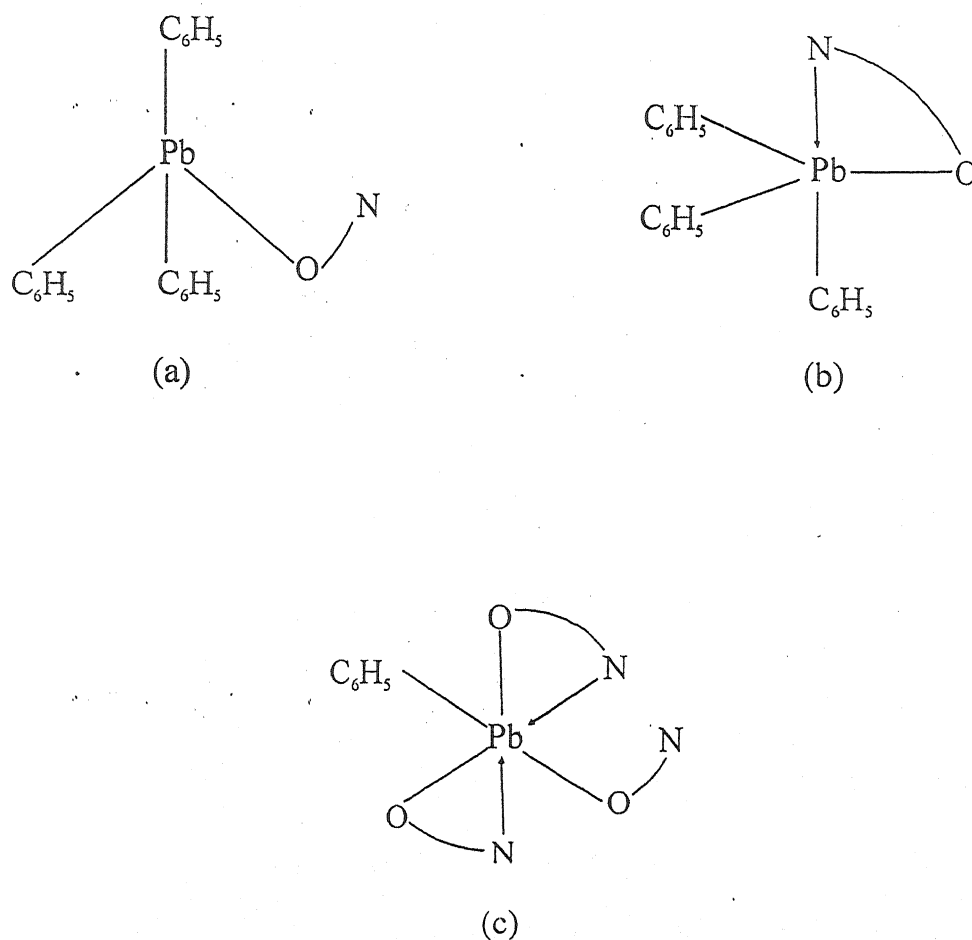
Fig.6.(a) Triphenyl-lead 8-oxyquinolinate in ethanol solution.(b) Triphenyl-lead 8-oxyquino-linate in benzene solution.(c) Monophenyltris(8-oxyquinolinate). (ON represents the oxygen and nitrogen coordination points in 8-oxyquinolinate).

(f) Carboxylates :

Th best-known carboxylate of lead(II) is lead (III) acetate, $(CH_3COO)_2Pb.3H_2O$ (Sugar of lead), made by dissolving lead(III) oxide in acetic acid. The salt is very soluble in water (1g dissolves in about 1.6ml of cold water or 0.5ml of boiling water). Solutions are only partly ionized, which accounts for the strong solvent effect of acetates upon lead compounds (Aqueous solutions of lead(II) acetate freely dissolve lead(II) oxide.)

$$Pb^{2+} + CH_3COO^- \longrightarrow CH_3COOPb^+ \qquad K_1 = 145$$

$$Pb^{2+} + 2CH_3COO^- \longrightarrow (CH_3COO)_2Pb \qquad K_2 = 810$$

$$Pb^{2+} + 3CH_3COO^- \longrightarrow (CH_3COO)_2Pb^- \qquad K_3 = 2950$$
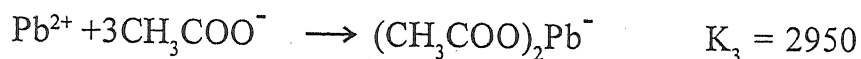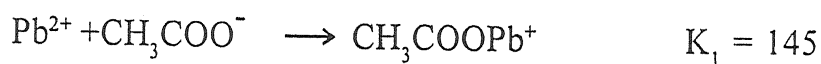
Lead acetate solutions absorb carbon dioxide from the air and precipitate insoluble carbonates.

Many other lead(II) carboxylates are known such as formate, propionate, butyrate, stearate, oxalate, tartrate, etc., many of which find industrial uses as lubricant additives varnish driers, silk weighing, etc[108].

Lead(IV) acetate is best made by the action of glacial acetic acid upon Pb_3O_4. The colourless crystals are very sensitive to moisture hydrolysing to lead(IV) oxide and acetic acid[109,110].

It is very extensively used as a selective oxidizing agent in organic chemistry.

Other lead(IV) carboxylates such as propionate, butyrate and stearate are known.

Organolead(IV) carboxylates of general formulae R_3PbO_2CR', $R_3Pb(O_2CR')_2$ and $RPb(O_2CR')_3$ are known. The equations below indicate some of the syntheses available[111-115].

$$R_4Pb + R'COOH \longrightarrow R_3PbO_2CR'$$
$$(C_2H_5)_4Pb + (CH_3COO)_4Pb \longrightarrow (C_2H_5)_3PbO_2CCH_3$$
$$(C_2H_5)_6Pb_2 + (C_6H_5COO)_2 \longrightarrow (C_2H_5)_3PbO_2CC_6H_5$$
$$R_3PbX + R'COOAg \longrightarrow R_3PbO_2CR'$$
$$R_3PbOH + R'COOH \longrightarrow R_3PbO_2CR'$$
$$R_2PbO + R'COOH \longrightarrow R_2Pb(O_2CR')_2$$
$$R_2PbX_2 + R'COOAg \longrightarrow R_2Pb(O_2CR')_2$$
$$R_2Pb(O_2CR')_2 + Hg(O_2CR')_2 \longrightarrow RPb(O_2CR')_3$$
$$(CH_3COO)_4Pb + R_2Hg \longrightarrow RPb(O_2CCH_3)_3$$
$$RPbO_2H + R'COOH \longrightarrow RPb(O_2CR')_3$$
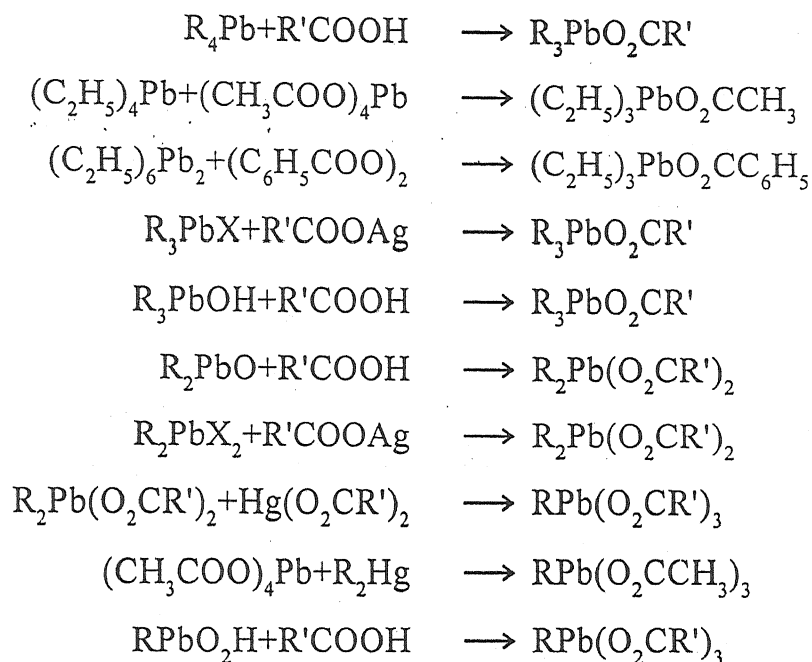
Very many organolead carboxylates have been investigated for potential commercial uses. Little structural information in available for these compounds, but the trimethyl-lead carboxylates are believed to be coordination polymers[116,117] in which planar trimethyl-lead ions are joined by carboxylates groups as in Fig.7 producing five-coordinate lead.
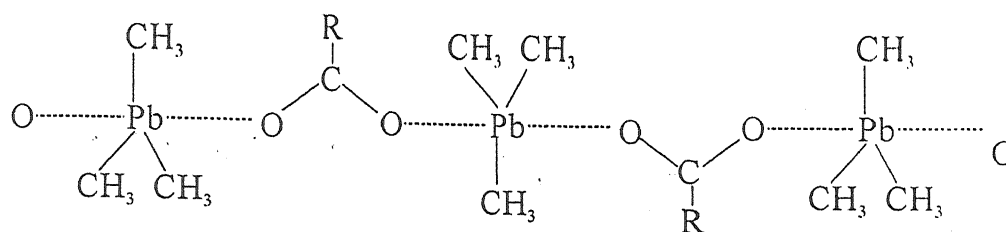
Fig.7. Polymeric trimethyl-lead carboxylates.

Organolead peroxides of type R_3PbOOR and $R_3PbOOPbR_3$ exist and are reasonably stable[118,119], but the peroxycarboxylates R_3PbO_3CR are very unstable and are not well characterized[120].

LEAD SALTS OF INORGANIC ACIDS

(a)   Sulphates, Selenates, Fluorosulphonates and

    Chlorosulphonate:

Lead(II) sulphate is precipitated from lead(II) solutions by sulphate ions, and is one of the popular gravimetric precipitates for lead. Its increased solubility in concentrated sulphuric acid suggests formation of sulphato or bisulphato complexes of lead(II). Lead selenate is precipitated similarly from Pb^{++} and SeO_4^{--} mixing.

Lead(IV) sulphate may be prepared by a number of methods. Concentrated sulphuric acid on either lead(IV) fluoride[121] or lead(IV) acetate produces $Pb(SO_4)_2$; and electrolysis of strong sulphuric acid with lead electrodes gives $Pb(SO_4)_2$ under carefully

controlled conditions[123]., $Pb(SO_4)_2$ is stable in dry air, but is hydrolysed to PbO_2 by moisture[123].

If an acid solution of $Pb(SO_4)_2$ is treated with alkali sulphate, salts such as $K_2Pb(SO_4)_3$ are obtained. No structural data are available for these salts, but they are likely to contain the $[Pb^{IV}(SO_4)_3]^{2-}$ anion[124].

Lead(IV) acetate dissolves in concentrated sulphuric acid to form hexa (hydrogen-sulphato) plumbic acid $H_2Pb(HSO_4)_6$, $H_2Pb(HSO_3)_6$ and $H_2Pb(ClSO_3)_6$ respectively.

The organometallic sulphates of lead(IV) are stable crystalline compounds made by the action of sulphuric acid upon the requisite organometallic oxide or hydroxide.

(b)   Nitrates :

Lead(II) nitrate is normally made by the action of nitric acid upon lead metal or lead(II) oxide. It is freely soluble in water, but contrary to the behaviour of most nitrates, it is incompletely dissociated in solution[126,127]. The $PbNO_3^+$ cation has a formation constant of 15.1 at infinite dilution at 25^0C.

$$Pb^{2+} + NO_3^- \longrightarrow PbNO_3^+ \qquad (K = 15.1)$$
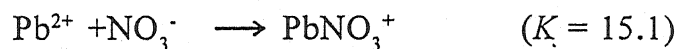
The formation constant of the reaction at ionic strength 2.0 is a approximately 2.6.

A number of basic nitrates of lead are known, and are discussed in the hydroxy section above.

Efforts to prepare lead(IV) nitrate or hexanitrato complexes of lead(IV) have, to date, been unsuccessful[128]. The organometallic nitrates of lead(IV) are, however, well known and crystalline specimens of such nitrates as $(C_2H_5)_3PbNO_3$, $(CH_3)_3PbNO_3$, $(C_6H_5)_3PbNO_3$, $(C_2H_5)_2Pb(NO_3)_2$, $(C_6H_5)_2Pb(NO_3)_2.2H_2O$ and $(p-CH_3.C_6H_4)_2Pb(NO_3)_2.3H_2O$ can be prepared by a variety of reactions.

$$(C_6H_5)_4Pb + HNO_3 \longrightarrow (C_6H_5)_2Pb(NO_3)_2.2H_2O$$

$$(C_2H_5)_4Pb + HNO_3 \longrightarrow (C_2H_5)_2Pb(NO_3)_2$$

$$(C_{12}H_{25})_3PbCl + AgNO_3 \longrightarrow (C_{12}H_{25})_3PbNO_3$$

$$(C_6H_5)_4Pb + Cu(NO_3)_2 \longrightarrow (C_6H_5)_2PbNO_3$$
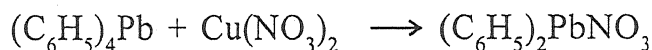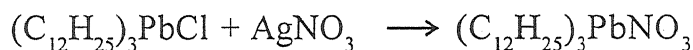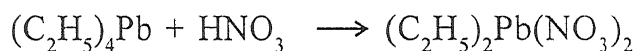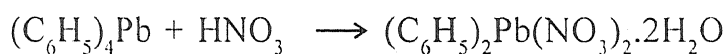
The Raman spectrum of an aqueous solution of dimethyl-lead dinitrate suggests that the dimethyl-lead cation has undissociated nitrate ion as well as water in its coordination sphere[129].

The action of N_2O_4 on lead tetra-alkyls produces the compounds formulated a $[R_4Pb(NO)_2](NO_3)_2$, in which the octahedral complex ion $[R_4Pb(NO)_2]^{2+}$ is believed present. Although the stoichiometry of this series of compounds is well established the structura formulation seems very dubious[130].

(c) Oxyhalogen Salts :

Lead(II) chlorite, chlorate, bromate, iodate and perchlorate are the known oxyhalogen salts of lead. $Pb(ClO_2)_2$ is made by the action of $Ba(ClO_2)_2$ solution upon lead nitrate solution[131]. The yellow crystals have a pseudotetragonal cell (a= 4.14 Å, c/a= 1.51)[132].

Lead(II) chlorite decomposes upon heating to a mixture of lead(II) chloride and lead(II) perchlorate, or alternatively to oxygen and lead(II) chloride depending upon the rate and intensity of heating.

Lead(II) chlorate is obtained as the hydrate $Pb(ClO_2)_2.H_2O$ from the dissolution of lead carbonate in aqueous chloric acid. The anhydrous chlorate is got by careful heating of the hydrate at 110-150°, but at higher temperatures decomposition to lead(II) chloride, lead(IV) oxide, chlorine and oxygen occurs, and the breakdown can be explosive.

Solutions of lead acetate and potassium bromate precipitate the less soluble lead bromate. It is possible for the double salt $Pb(BrO_3)_2. Pb(OCOCH_3)_2$ to be formed in this preparation and this double salt explodes violently at about 165°, or even at room temperature upon percusion. Two fatal accidents have occurred by explosions of $Pb(BrO_3)_2$ due to the double salt impurity

present, and lead(II) bromate prepared in this way should be treated with extreme care[133]. An alternative synthesis involves treatment of lead carbonate with bromic acid to form $Pb(BrO_3)_2.H_2O$ [134].

Lead iodate precipitates as the anhydrous salt from lead(II) solutions and alkali iodate solutions. It is thermally more stable than the chlorate or bromate, and only decomposes a 250-300°.

The variation of the aqueous solubilities of lead(II) chlorate, bromate and iodate at remarkable. 1 ml of water at 18°C will dissolve 4.4g of $Pb(ClO_3)_2$, 1.3×10^{-2} g of $Pb(BrO_3)_2$ and 1.9×10^{-5} g of $Pb(IO_3)_2$.

$Pb(ClO_3)_2.3H_2O$ (m.p. 84°) is made by the dissolution of lead carbonate in queous perchloric acid[135]. The monohydrate m.p. 153-155° is also known.

(d)   Phosphites and Phosphates :

The phosphate of lead(IV) formulated as $Pb(H_2PO_4)_4$ was synthesized electrolytically from lead electrodes and strong phosphoric acid. It is formed as white crystals which a stable in the air, and it behaves as a slow but fairly strong oxidizing agent, releasing iodide from potassium iodide.

The corresponding monoacid phosphate of lead(IV),

$Pb(HPO_4)_2$ was made by the action of phosphoric acid upon lead(IV) acetate[137].

Lead(II) hypophosphte $Pb(H_2PO_2)_2$ was prepared by dissoluton of lead(II) oxide[138] or lead carbonate[139] in hypophosphorous acid, or alternatvely by metathesis between lead(II) nitrate and calcium hypophosphate. It is slightly soluble in cold water to give a feebly acidic solution, but is much more soluble in hot water. On treatment of $Pb(H_2PO_2)_2$ with a strong solution of lead nitrate, it forms the nitrohypophosphite $Pb(H_2PO_2)NO_3$, which behaves as a detonant[140].

The neutral hypophosphite $Pb_2P_2O_6$ has been characterized by its infrared spectrum[141] over the region 4000-650 cm^{-1}.

The phosphite $PbHPO_3$ may be obtained by the metathesis of lead nitrate or lead acetate with alkalic phosphite, or alternatively by the partial neutralization of phosphorous acid solution with lead carbonate. When $PbHPO_3$ is dissolved an a warm concentrated solution of phosphorous acid the acid phophite $Pb(H_2PO_3)_2$ is obtained, and can be isolated a large transparent crystals[142].

Certain basic phosphite formulated a $2PbHPO_3.2PbO.H_2$, $PbHPO_3. 2PbO.\frac{1}{2}H_2O$ and $PbHPO_3.$

2PbO.½H$_2$O have also been reported, though the stoichiometries may be dubious. In addition, halogenophophites and nitratophosphite PbPO$_3$F, PbHPO$_3$. PbCl.H$_2$O, PbHPO$_3$. 2PbBr$_2$.H$_2$O and PbHPO$_3$.Pb(NO$_3$)$_2$ are claimed[142].

Melts of phosphorus(V) oxide and lead(II) oxide containing less than about 65% molar of lead(II) oxide form glasses, and are not discussed with the discrete phosphates of lead outlined below.

Lead(II) metaphosphates formulated as dimetaphosphate Pb(PO$_3$)$_2$, trimetaphosphate ½[Pb$_3$(PO$_3$)$_6$.3H$_2$O], tetrametaphosphate Pb$_2$(PO$_3$)$_4$ and hexametaphosphate Pb$_3$(PO$_3$)$_6$ have been claimed. Preparations usually involve the action of alkali metaphosphate upon soluble lead(II) salts, but conditions appear to be critical for obtaining the right product[147,148,149]. Fusion methods involving lead nitrate and phosphorus(V) oxide have also been used[150].

The three orthophosphates of lead are well characterized and have been extensively studied.

PbHPO$_4$ exists in nature as the mineral monetite (density 5.66g/cc), which is monoclinic (a =4.66 Å, b = 6.64 Å, c = 5.77 Å, β =83^0), the unit cell containing two PbHPO$_4$ units[151].

PbHPO$_4$ is only slightly soluble in water, and

disproportionates to the phosphate $Pb_3(PO_3)_2$ and phosphoric acid on boiling in water. $PbHPO_4$ is transformed to the pyrophosphate $Pb_2P_2O_7$ on heating. The decomposition starts at about 195^0 and probably proceeds via the tetrametaphosphate of lead.

$PbHPO_4$ may be synthesized from lead nitrate and phosphoric acid in the right conditions[152].

Phophoric acid dissolves $PbHPO_4$ to form $Pb(H_2PO_4)_2$. This lead diacid phosphate is stable in the air but decomposed by water. A number of compounds of the type $Pb(HRPO_4)_2$, where R is CH_3, C_2H_5, C_3H_7, etc. are also known[153].

Lead orthophosphate $Pb_3(PO_4)_2$ may be prepared in a number of ways. $Pb_3(PO_4)_2$ the product of the neutralization of $PbHPO_4$ with ammonia[154], and lead(II) chloride and Na_2HPO_4 give $Pb_3(PO_4)_2$ [155]. The solubility of lead orthophosphate in water is 1.35×10 g/l. at 20^0. $Pb_3(PO_4)_2$ is dimorphic[156] with a transition point at 782^0, andit melts at 1104^0.

Various apatites of lead are known[156-160] with the general stoichiometric $3[Pb_3(PO_4)_2].PbX_2$ where X = F, Cl, Br, I and OH. These apatites of lead form a homgeneous crystallographic group in the same way as the better-known apatites of calcium. The chloroapatite $3[Pb_3(PO_4)_2].PbCl_2$ occurs in nature as the mineral pyromorphi (density 7.01g/cc, dielectric constant 47.5at = 75cm).

A mixed hydroxyapatite of calcium and lead $Ca_5PB_5(PO_4)_6(OH)_2$ (density 5.39 g/cc) hexagonal with a = 9.62 Å and c = 7.08 Å[161].

Many arsenites and arsenates comparable to the above phosphites and phosphates has been characterized[162].

(e)   *Carbonates :*

Lead carbonate $PbCO_3$ occurs in nature as the mineral cerusite. It may be prepared the action of alkali carbonate upon a solution of lead acetate or nitrate, but the preparatic must be kept cold in order to avoid formation of the the basic carbonate. Another method preparation of the neutral carbonate involves shaking a cold solution of sodium carbonate with a suspension of a salt of lead which has a low solubility, but which is not as insoluble as lead carbonate itself[163]. Chloride, bromide and sulphate have been utilized in this content.

$PbCO_3$ as cerusite is orthorhombic and is isomorphous with aragonite $CaCO_3$, strotianite $SrCO_3$ and witherite $BaCO_3$.$PbCO_3$ has a density 6.58 g/cc and a unit of a = 5.195 Å, b = 8.436 Å and c = 6.152 Å[164].

Lead carbonate appears to undergo slight decomposition on exposure to strong light and is decomposed to carbon dioxide and lead(II) oxide on heating, thus at 184⁰, for example has a

dissociation pressure of 10mm of mercury. Decomposition starts at about 130^0 and is complete at about 470^0 [166].

$PbCO_3$ has a solubility product in pure water of 3.3×10^{-14}, but the solubility is much increased by the presence of carbon dioxide in the water, even in quite small amounts[167].

The halogenocarbonates $PbCl_2.PbCO_3$ and $PbBr_2.PbCO_3$ are isomorphous[168,169], but the coresponding iodide could not be made. The chlorocarbonate $PbCl_2.PbCO_3$ is present in nature as the mineral phosgenite, and can be made by the action of phosgene upon lead hydroxide or by the action of carbon dioxide upon a solution of lead chloride. Natural and synthetic phosgenite have been shown to have identical crystal structures.

In the thermal decomposition of lead carbonate it is believed that the basic carbonates $PbO.PbCO_3$, $2PbO_3.PbCO_3$ and $3PbO_2.5PbCO_3$ are formed as intermediates[166,170], but the very well-characterized basic carbonate is the hydroxycarbonate $Pb(OH)_2.2PbCO_3$, the mineral hydrocerusite. The basic carbonate $Pb(OH)_2.2PbCO_3$ can be made by the action of urea and water upon basic lead acetate. In a sealed tube at 130^0 the urea is converted to ammonium carbonate, which precipitates $Pb(OH)_2.2PbCO_3$ as fine hexagonal crystals[171]. The hydroxycarbonate $3PbCO_3.Pb(OH)_2$ has been characterized by X-ray crystallography, and is made by passing air into an alkaline solution of lead acetate[172].

CHALCOGEN COMPOUNDS

(a)   Sulphides :

Lead(II) sulphide crystallizes in a perfect NaCl structure[173] with Pb-S distance 2.97Å, and is the only binary sulphide of lead. It is found in nature as large regular crystals of galena. It has a grey-blue metallic character and density about 7.6. It is best synthesized in a crystalline form by the action of thiourea upon sodium plumbite solution[174].

PbS is a *p*-type semiconductor when sulphur rich and an n-type semiconductor when lead rich. A conductivity of 1.3×10^{-4} $^{-1}$ cm^{-1} is found for stoichiometric PbS[175]. Crystalline PbS is a remarkable radio detector, and was widely used in early crystal radio receivers.

Lead sulphide sublimes unchanged[176] and has a vapour pressure of about 20 mm of mercury at 1000^0C, and boils at about 1200^0C. It is exceedingly insoluble in water (solubility product about 8×10^{-28} at 25^0C)[177], but it is attacked by strong acids.

Very many organolead compounds containing covalent lead-sulphur bonds are known with general formulae R_3PBSR', $R_2Pb(SR')_2$, $R_3PbSPbR_3$, etc., in which lead(IV) is present. Some synthetic routes to these types are outlined below[178].

$$(C_2H_5)_3PbOH + (NH_2)_2CS \longrightarrow (C_2H_5)_3PbSPb(C_2H_5)_3$$

$$R_3PbOH + R'SH \longrightarrow R_3PbSR'$$

$$(C_2H_5)_4Pb + S \longrightarrow (C_2H_5)_3PbSPb(C_2H_5)_3$$

$$(C_6H_5)_3PbSLi + (C_6H_5)_3SnCl \longrightarrow (C_6H_5)_3PbSSn(C_6H_5)_3$$
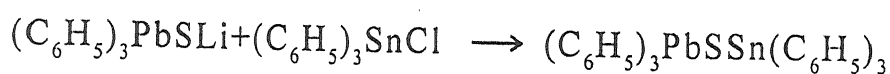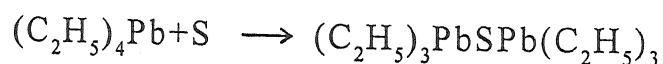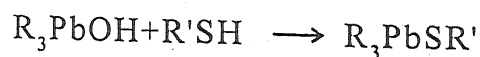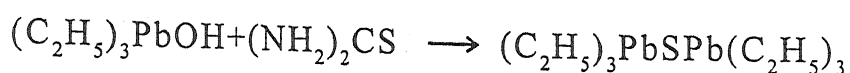
All these sulphur derivatives of lead(IV) are considerably less stable than the sponding compounds of tin, germanium and silicon[178].

Lead, however, is unique in Group IVB in forming stable lead(III) thiolates. These formed instantly as yellow crystalline precipitates by the direct action of thiols upon tions of lead(II) salts. These lead mercaptides form yellow crystals with sharp melting which are soluble in many organic solvents[179]. Whilst no structural data are available, compounds appear to be convalent thiolates of lead(II).

Lead(II) mercaptides have been widely used as intermediates.

$$(CH_3S)_2Pb + CH_3COCl \longrightarrow CH_3COSCH_3$$

$$(RS)_2Pb + BrCH_2CH_2COONa \longrightarrow RSCH_2CH_2COONa$$
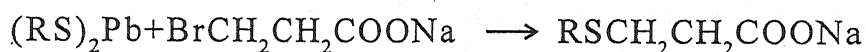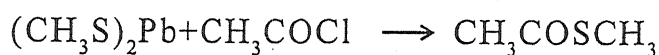
They are oxidized in the air or by iodine to produce the corresponding disulphide nitric acid produces the corresponding sulphonic acid.

$$(RS)_2Pb + O \longrightarrow R_2S_2 + PbO$$

$$(RS)_2Pb + I_2 \longrightarrow R_2S_2 + PbI_2$$
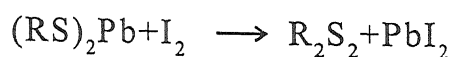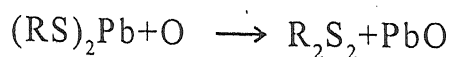
At about 200° the lead(II) mercaptides disproportionate to the organic sulphide an sulphide[179].

$$(RS)_2Pb \longrightarrow R_2S + PbS$$
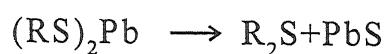
(b)   Selenides :

Thermal and X-ray analysis, and other physical methods have shown that PbSe only compound formed in the lead-selenium system[180]. PbSe is a lead-grey m.p. 1065°, with a cubic NaCl lattice (a = 6.12 to 6.15 Å from various determina PbSe occurs in nature as the mineral clausthalite, which is isomorphous with galena selenide is synthesized by the interaction of stoichiometric quantities of the element 1200-1250°, with subsequent annealing in argon at 800° [181], It can also be made by the of hydrogen selenide upon lead salts, but some free selenium is liberated during the rea lead selenide is precipitated from a solution of lead acetate and selenourea or hydrazine. Purification of PbSe can be carried out by vacuum distillation at 10^{-6} m or alternatively by zone refining. When PbSe crystals are grown from a melt contained small excess of selenioum or lead, the semiconductor (5×10^{-2} to 5×10^{-3} ohm cm) crystals will have respectively hole or electron conductivity[180].

Films of lead selenide up to 1000 Å thick are completely oxidized to $PbSeO_3$ in 350⁰ after 10 min; bulk samples oxidize more slowly. The photoconductivity of lead is sensitive to the content of oxygen and other elements in the deposited film[180], sensitivity is in the range 3-10 , and increases with reduction of temperature[182].

Few organic lead-selenium compounds are known, but organolead selenolates such as $(CH_3)_3PbSeR$ are known, as also are examples of the hexa-aryldilead selenides $(R_3Pb)_2Se$ [178]. The lithium salts $(C_6H_5)_3PbSeLi$ are formed in an interesting manner by the direct attack of selenium upon the lithium triaryl-lead.

$$(C_6H_5)_3PbLi + Se \longrightarrow (C_6H_5)_3PbSeLi$$

(c)   Tellurides :

PbTe is the sole telluride of lead and occurs in nature as the mineral altaite. It may be synthesized by high-temperature reaction of stoichiometric quantities of the elements, or by the action of tellurium powder on a boiling solution of lead salt.

PbTe melts at 860⁰. It behave as a semiconductor of the n- and p-types depending upon which component is present in slight exces. PbTe displays photoconductivity at low temperatures[183].

The mixed telluride Pb_xSn_{1-x} Te shows potential as a tuneable long-wavelength laser under variable temperature and pressure[184].

Organolead tellurides are very rare and appear to be currently restricted to $[(C_6H_5)_3Pb]_2Te$ (m.p. 129°) and its lithium salt $(C_6H_5)_3PbTeLi$ [178].

HALOGENO COMPOUNDS

(a) Lead(II) Halides

Lead(II) fluoride is obtained a a white crystalline powder by dissolving lead carbonate in hydrofluoric acid and decomposing the hydrofluoride formed by rapid melting. Alternatively it is prepared from lead metal and anhydrous hydrofluoric acid at 160°, under autogenous pressure.

Lead(II) fluoride is dimorphic, the low-temperature rhombic PbF_2 form having the $PbCl_2$ structure and the high-temperature (above 316°C) form having the cubic fluorite structure[185].

Lead(II) chloride, bromide and iodide are all prepared by addition of the requisite halide to solutions of lead(II) ion. Lead(II) chloride and bromide are white like the fluoride, and lead(II) iodide forms bright yellow very characteristic haxagonal plates. The solubilities of the lead(II) halides in water increase markedly on heating.

In crystalline $PbCl_2$ and $PbBr_2$ each lead atom is

coordinated by nine halide ions, six of which lie at the apices of a trigonal prism, with the remaining three beyond the centres of the three prism faces. PbI_2 has the CdI_2 layer structure[186].

Electron diffraction measurements of the vapours of $PbCl_2$, $PbBr_2$ and PbI_2 show them as angular molecules, with bond lengths. Some doubt, however, has been cast upon the existence of PbX_2 molecules in the vapour state[187].

Freezing point curves and conductimetric studies of mixtures of lea(II) halides show the existence of a variety of mixed halides such as PbFCl, PbFBr, PbFI, $PbCl_2.4PbF_2$ and $PbBr_2.4PbF_2$.

Lead(II) chlorofluoride is sparingly soluble in water, and is the precipitate deposited when a lead salt is added to a solution containing both fluoride and chloride ions. This precipitation of PbFCl is the bais of an important analytical method for the determination of fluoride. PbBrF is also only very sparingly soluble in water.

PbFCl and PbFBr have a tetragonal complex layer structure.

(b) Lead(IV) Halides

Only lead(IV) fluoride and chloride are known. The non-exitence of lead(IV) bromide and iodide can be put down to the

reducing power of Br⁻ and I⁻ or, stated alternatively, the inability of bromine and iodine to oxidize lead (II).

Lead(IV) fluoride is obtainedby the direct fluorination of lead(II) fluoride at about 300^0 [188]. It is formed as white needles which are very sensitive to moisture, immediately decolorizing due to the formation of brown PbO_2. PbF_4 has a tetragonal cell (a = 4.24 Å and c = 8.03 Å).

Lead(IV) chloride is a clear yellow highly refracting liquid which fumes in moist air, and under certain circumstances decomposes explosively to lead(II) chloride and chlorine. It is best prepared by the action of concentrated sulphuric acid upon pyridinium hexachloroplumbate, and stored under pure concentrated sulphuric acid at -80^0 in the dark[189].

(c) Coordination Complexes of Lead Halides

An early report indicates[190] the following coordination complexes of lead(IV) chloride: $PbCl_4(NH_3)_2$; $PbCl_4(NH_3)_4$; $PbCl_4(CH_3NH_2)_4$; $PbCl_4(C_2H_5NH_2)_4$; $PbCl_4(C_3H_7NH_2)_4$; $PbCl_4(C_6H_5NH_2)_3$; $PbCl_4(C_5H_5N)_2$.

No structural information is available upon these complexes, but the L_2PbCl_4 types are likely to contain six-coordinate octahedral lead, and the L_4PbCl_4 types may contain eight coordinate lead[191].

The complex bix(thiourea) $PbCl_2$ is of some interest as a coordination complex of lead(II) chloride. Each lead atom is in a distorted trigonal prism environment of four sulphur atoms (Pb-S = 3.02 Å) and two chlorine atoms (Pb-Cl = 2.75 Å). Lead may, however, be regarded as seven-coordinate rather than six-coordinate as each lead atom also has a chlorine near the centre of a lateral face of the trigonal prism (Pb-Cl = 3.22 Å)[192].

(d)   Halogenolead(II) Ions

Solutions of lead(II) halides contain the PbX^+ ion in addition to the Pb^{2+} and X^- ions. The thermodynamics of these ion dissociations have been investigated by conductimetric methods[193].

Alkali fluorides and lead(II) fluoride form alkali fluoroplumbites. In the case of potassium the compound formed is K_4PbF_6, but in the cases of rubidium and caesium the compounds have stoichiometry $MPbF_3$ with perowskite structures[194].

The solubilities of lead(II) chloride, bromide and iodide decrease at first in the presence of halide ion, due to the common ion effect, but with further halide ion the solubility rapidly increases with the formations of complex ions.

From aqueous crystallizations and phase studies on mixed salt systems, a quite remarkable number of solid state stoichiometries have been obtained for the halogenoplumbites.

Representative of these are KPb_2Cl_5, K_2PbCl_4, $CsPbCl_3$, $RbPbCl_3$, $KPbBr_3$, $KPbI_3$, Cs_4PbCl_6, K_4PbF_6, K_4PbCl_6 and K_4PbBr_6.

Spectroscopic measurements on $PbCl_2$-Cl^- solutions do not permit positive identification of $PbCl_3^-$ and $PbCl_4^{2-}$, but the limiting spectrum of $PbCl_2$ in 11 M hydrochloric acid is believed due to $PbCl_6^{4-}$ in solution[195].

It is likely that the PbX_3^- ions are pyramidal like the corresponding SnX_3^- ions. The pale yellow $KPbI_3.2H_2O$ is particularly well known, and is formed when warm aqueous solutions of lead nitrate and potassium iodide are mixed. The complex is somewhat weak, and renewed heating causes dissociation to potassium iodide and lead(II) iodide. Anhydrous white $KPbI_3$ is formed by storing the dihydrate over concentrated sulphuric acid or by dissolving $KPbI_3.2H_2O$ in acetone (in which it is quite soluble), and precipitating with ether.

Anhydrous $KPbI_3$ is curious, in that when reattacked by water it immediately forms bright yellow lead(II) iodide rather than $KPbI_3.2H_2O$. This reaction is used for the detection of traces of water in gases or organic solvents. The stabilities of the halide complexes of lead [193-196] are in the order $I^- > Br^- > Cl^- > F^-$; no fluoride complexes are detectable in solution. It is believed that chlorine, bromine and iodine utilize *d*-orbitals for partial double bonding to lead in these complex ions[197].

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In the salt $NH_4Pb_2Br_5$ the lead atom has two nearest bromine neighbours at 2.98 Å, two bromine at 3.16 Å and four bromines at 3.35 Å. It would appear to consist of discrete NH_4^+ and Br^- ions alongwith $PbBr_2$ molecules. The Br-Pb-Br angle in the $PbBr_2$ units is ~85.5⁰, and the Pb-Br bond length at 2.98 Å is about half-way between convalent and ionic distance for Pb-Br[198].

The salts K_4PbF_6, K_4PbCl_6 and K_4PbBr_6 are remarkable in having PbX_6^{4-} octahedral anions[199].

(e) Halogenolead(IV) Ions

The hexafluoroplumbates M_2PbF_6 are prepared either by dissolution of alkali plumbate in hydrofluoric acid, or by neutralizing an alkali metal carbonate with a solution of PbF_4 in hydrofluoric acid.

The salt K_3HPbF_8 has been prepared in a number of ways, such as adding lead tetraacetate to a solution of potassium fluoride in hydrofluoric acid, or by dissolving a fusion of lead(IV) oxide and alkali in hydrofluoric acid. The well-defined crystals are made up of K^+, HF_2^- and PbF_6^- ions[200].

The alkaline earth salts $MPbF_6$ present an interesting series of structural changes. $CaPbF_6$ contains no discrete complex ions, but consists of a superstructure of the ReO_3 type[201]. $SrPbF_6$ contains linear polymeric complex ions of the type $(PbF_5)_n^{n-1}$ along

with F-ions, and $BaPbF_6$ has discrete PbF_6^{2-} ions. The alkaline earth fluoroplumbates were made by the direct fluorination of the plumbates $MPbO_3$.

The hexachloroplumbate salts M_2PbCl_6 represent a convenient and stable source of lead(IV). A solution of H_2PbCl_6 is easily produced by the action of chlorine upon a fine suspension of lead(II) chloride in concentrated hydrochloric acid. Subsequent addition of solutions of either ammonium or potassium chloride produces the corresponding M_2PbCl_6 salt as lemon yellow crystals. The alkali hexachloroplumbates are isomorphous with the hexachlorostannates.

(f) Organolead Halides

Compared with the other Group IVB organometallic halides, knowledge of organolead halides is somewhat sparse[24,25,26,202]. The types R_3PbX and R_2PbX_2 are well characterized, but compounds of formula $RPbX_3$ are practically unknown.

The usual method for the preparation of organolead halides is by the action of hydrogen halides upon tetra-organoleads. Initial reaction involves fission of one carbon-lead bond, with loss of a further alkyl/aryl group under more vigorous conditions.

$$R_4Pb + HX \longrightarrow R_3PbX + RH$$

$$R_3PbX + HX \longrightarrow R_2PbX_2 + RH$$
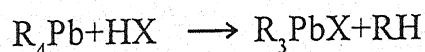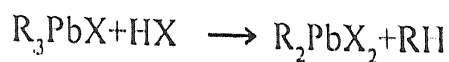
The trialkyl- and triaryl-lead halides R_3PbX in which X is chlorine, bromine, or iodine have all been prepared in this way at low temperature in a solvent. At higher temperatures the principal product is the di-alkyl- or di-aryl-lead halide.

Halogenation by metal and other halides and by the halogens themselves, has proved to be useful synthetic routes from the tetra-organoleads to the organolead halides in various special cases[203, 204].

$$(C_6H_5)_4Pb + 2AlCl_3 \longrightarrow (C_6H_5)_2PbCl_2 + 2C_6H_5AlCl_2$$

$$R_4Pb + SOCl_2 \longrightarrow R_3PbCl + RSOCl \ (R = alkyl)$$

$$Ar_4Pb + SOCl_2 \longrightarrow Ar_2PbCl_2 + Ar_2SO$$
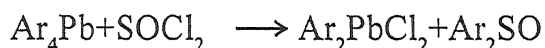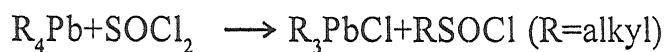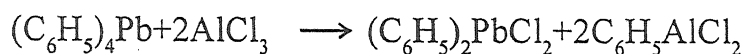
Although at first appearing an unattractive route, the fission by halogens of the lead-lead bond in hexa-alkyl-dileads is in fact an economic route to the trialkyl-lead halides[202]. This is a result of the formation of the hexa-alkyl dileads as cheap by-products of the commercial synthesis of the antiknock tetra-alkyl-leads.

$$R_3Pb.PbR_3 + X_2 \longrightarrow 2R_3PbX \quad (R = alkyl, X = Cl, Br \ and \ I)$$
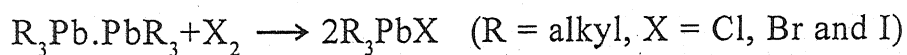
The attractive proportionation reaction between tetra-organotins and tin(IV) tetrahalides for the preparation of organotin halides is of little use in organolead chemistry, as the low thermal

stability of organolead halides and the lead(IV) halides does not allow the temperature range of these proportionations to be reached, except in a few special cases[205].

One of the more important synthetic methods for the preparation of the organometallic halides of silicon, germanium, and tin is the "direct" reaction between organic halide and metal. All efforts to use this approach for the preparation of the organolead halides have been entirely unsuccessful.

The fluorides are best prepared by the action of alkali fluorides upon organolead halides, or hydrogen fluoride upon alkyl-lead hydroxides[206].

$$(C_6H_5)_3PbBr+KF \longrightarrow (C_6H_5)_3PbF+KBr$$
$$(CH_3)_3PbOH+HF \longrightarrow (CH_3)_3PbF+H_2O$$

The sole examples of the halides $RPbX_3$ reported to date are obtained by partial alkylation of $CsPbCl_3$ with alkyl halide[207].

Definitive structural information on the organolead halides is extremely sparse, and structural determinations would be desirable. Most readily in strongly halides have low solubilities in non-polar organic solvents, but dissolve more readily in strongly polar solvating solvents. The fluorides behave as ionic salts, but early suffestions that other organolead halides are also largely ionic have not been borne out. Thus trimethyl-lead chloride and tri-ethyl-

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lead chloride are non-conducting in tetramethylene sulphoxide[208].

Infrared data on the halides $(CH_3)_3PbX$ suggest a chain like constitution involving halogen bridges between lead atoms[209].

An X-ray crystal structure determination of diphenyl-lead dichloride showed it to have a linear polymeric structure as shown in Fig.8. There is an octahedral coordination about each lead atom, and all the chlorine atoms are bridging in character[210].
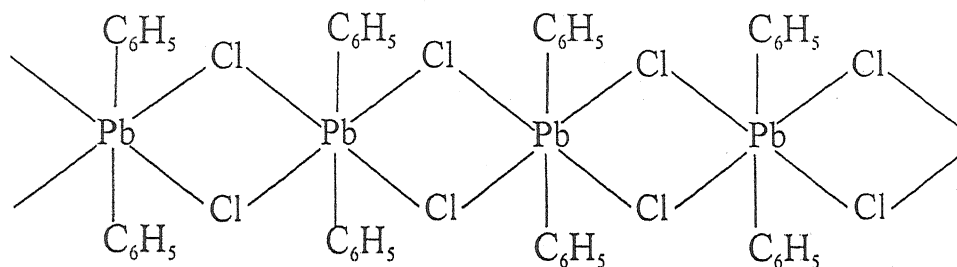
Fig.8. Structure of $(C_6H_5)_2PbCl_2$ in the crystal.

The monohalides R3PbX have an unpleasant smell, and the lower trialkyl-lead halides are extremely sternutatory and should be handled with care.

The organometallic halides are the starting point of most organometallic syntheses involving lead, and the halogen atom or atoms may be replaced by a great variety of other atoms and groups.

Borohydrides[211] and aluminohydrides[212] react with organolead halides to form the hydrides R_3PbH and R_2PbH_2, but

due to the very low thermal stability of the products, such reactions must be carried out at very low temperatures.

$$(CH_3)_3PbBr + KBH_4 \longrightarrow (CH_3)_3PbH$$
$$(CH_3)_2PbCl_2 + LiAlH_4 \longrightarrow (CH_3)_2PbH_2$$
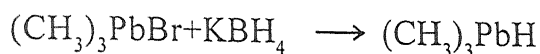
Metallation of the organolead halides by lithium sodium or potasium yields the synthetically useful metal tri-organoleads, whose exact nature is presently not fully understood.

Under suitable conditions the action of sodium upon the organometallic lead halides produces a Wurtz type of reaction andthe formation of the hexa-organodileads. The tri-organolead chlorides are reduced to the hexa-organodileads by aluminium in dilute potassium hydroxide solution[213].

In addition to the reactions involving the fission of the lead-halogen bond, the organolead halides undergo coordination reactions in which they remain intact, but undergo changes of stereochemistry due to the incoming ligand. $(CH_3)_3PbCl$ and $(C_2H_5)_3PbCl$ both form 1:1 complexes with tetramethylene sulphoxide, dimethylacetamide and dimethyl-formamide, in which the oxygen atoms bond to lead to give a trigonal bipyramidal structure with a planner tri-alkyl lead unit[208].

Diphenyl-lead dichloride complexes with such ligands as pyridine (1.2), dimethylsulphoxide (1:2), 1,1'-dipyridyl (1:1), and

ortho-phenanthroline (1:1) to produce octahedral complexes[214] as shown in fig.9.

(a)   (b)
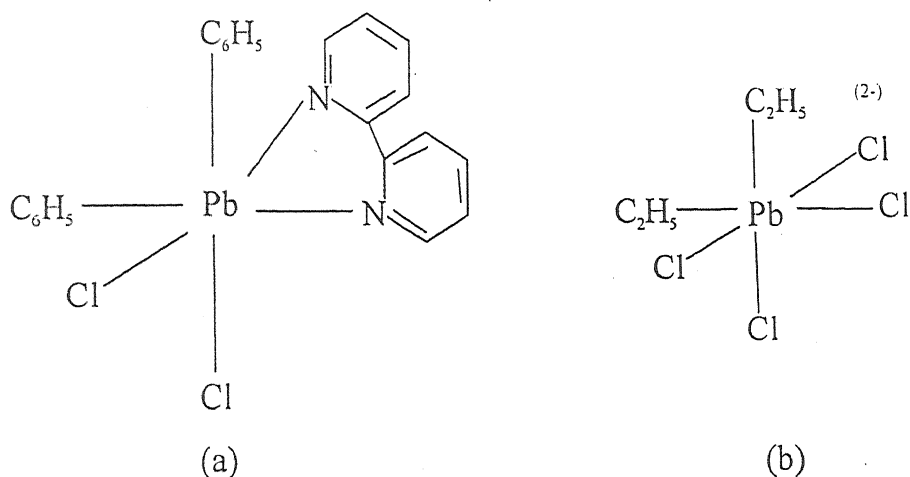
Both tri-organolead halides and di-organolead dihalides complex with halide ions to produce trigonal bipyramidal and octahedral complex anions uch as $[C_6H_5)_3PbCl_2]^-$, $[C_2H_5)_3PbCl_3]^{2-}$, $[C_2H_5)_3PbCl_2]^-$ and $[C_2H_5)_2PbCl_4]^{2-}$.

PSEUDOHALIDES

(a)   Thiocyanates and Selenocyanates

Lead(II) thiocynanate is precipitated from lead(II) solutions by potassium thiocyanate solution; a very pure form is obtained form lead nitrate. It is light-sensitive, and it decomposes at about 190^0C^{215}.

Lead(II) thiocyanate has a structure of particular interest. Each lead atom is eight-coordinate with two pairs of

sulphur atoms (at 3.05 and 3.14 Å) and two pairs of nitrogen atoms (at 2.70 and 2.72 Å), all from different thiocyanate ions. Further, all thiocyanate ions are bridging, and each thiocyanate ion makes contact with four lead(II) ions- two at each end. The thiocyanate ion is effectively linear with S-C 1.53 Å and C-N 1.26 Å[216].

Lead(IV) isothiocyanate has been reported from the action of the acid upon lead tetra-acetate. $Pb(NCS)_4$ undergoes very ready disproportionation to thiocyanogen and lead(II) isothiocyanate, and has consequently been little investigated[217].

The Corresponding organometallic derivatives of lead(IV), R_3PbNCS and $R_2Pb(NCS)_2$, are, however, much more stable and more extensively studied [218,219]. The isothiocyanato linkage Pb-N=C=S is believed present in these complexes from spectroscopic evidence, and a full asignment of the infrared spectrum of $(CH_3)_3PbNCS$ has been made. In contrast, however, the selenocyanate $(C_6H_5)_3PbSeCN$ is believed to have the normal Pb-Se-C=N attachment rather than the iso alternative[220].

(b) Isocyanates

Only organometallic isocyanates of lead(IV) R_3PbNCO (R= CH_3 and C_2H_5) are known[218,219].

$$(C_2H_5)_3PbCl+KOCN \longrightarrow (C_2H_5)_3PbNCO$$
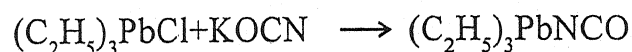
These are believed to contain metal-Nitrogen rather than metal oxygen bonds[218].

The triphenyl-lead fulminate $(C_6H_5)_3PbCNO$ is reported to rearrange to the isocyanate $(C_6H_5)_3PbCNO$ at $174°$ [221].

(c)   Cyanides

Lead(II) cyanide has been little studied[222,223] and although a compound has been formulated as $Pb(CN)_2$, there is considerable doubt about its true nature. The action of hydrocyanic acid upon lead(II) salts has been variously reported as producing $Pb(CN)_2$ and $Pb(CN)_2PbO$.

Organometallic cyanides of lead(IV) however, are well known[112,224,225].

$$R_3PbCl+KCN \longrightarrow R_3PbCN$$

$$R_3PbOH+HCN \longrightarrow R_3PbCN$$

$$R_3PbOH+NaCN \longrightarrow R_3PbCN$$

$(C_6H_5)_3PbCN$ is reported stable up to $250°C$.

(d)   Azides

Azides of lead are known for both Pb(II) and Pb(IV) states.

Lead(IV) azide was made by the action of hydrazoic

acid upon Pb_3O_4. The red solution of $Pb(N_3)_4$ fades rapidly and the product was not isolated, though nitrogen was evolved and $Pb(N_3)_2$ was deposited.

Highly explosive red crystals were deposited by the action of $(NH_4)_2PbCl_6$ upon sodium azide solution and, though not analysed a lead(IV) complex azide was believed present[226]. The types R_3PbN_3 and $R_2Pb(N_3)_2$ are obtained by the action of hydrazoic acid upon R_3PbOH or R_2PbO.

Triphenyl-lead azide melts without decomposition at 180^0. and is the least thermally stable of the Group IV triphenylmetal azides; the products of decomposition are $(C_6H_5)_4Pb$ and nitrogen[218].

Lead(II) azide is dimorphic. The slow diffusion of lead nitrate and sodium azide produce a monoclinic (β) form ($a = 5.09$ Å, $b = 8.84$ Å and $c = 17.51$ Å), whilst the α-form precipitated on mixing solutions of alkaline azides and lead(II) salts, and is orthorhombi ($a = 6.63$ Å, $b = 11.31$ Å and $c = 16.24$ Å). The α-form is converted to the β-form by the action of light, but may be preserved for years in the dark.

Both α- and β-forms of lead(II) azide are very senitive to shock and to thermal become position, but the activation evergy for decomposition of the β-form is considerably lower than that of

the α-form, and at about 260⁰C the violence of detonation of the β–form is above twenty times greater than that of the α-form[227].

Lead(II) azide has a very low solubility (solubility product at $20^0C = 2.58 \times 10^{-9}$), but decomposed by dilute nitric and dilute hydrofluoric acid.

Lead(II) azide is an extraordinarily treacherous compound, and should be handled with great respect. Explosive decomposition is catalysed by small quantities of impurities.

Various basic azides such a $PbN_6.PbO$ and $(PbN_6)_3(PbO)_5$ have been characterized by X-rays from suspensions of lead azides and oxides[228].

METAL-METAL BONDS CONTAINING LEAD

Alkali Metal Derivatives

Alkali metal derivatives of the type R_3PbM are most stable for R=aryl and M=lithium though many others are used in situ in reactions without being isolated [24, 26].

$$R_3Pb.PbR_3 + Na \xrightarrow{NH_4} R_3PbNa$$

$$(C_6H_5)_2PbBr_2 + Li \xrightarrow{NH_4} (C_6H_5)_2PbLi_2$$

$$PbCl_2 + LiR \longrightarrow R_3PbLi$$

$$R_4Pb + Na \xrightarrow{NH_4} R_3PbNa$$
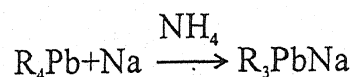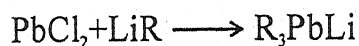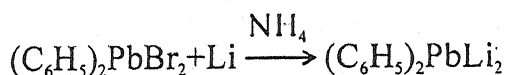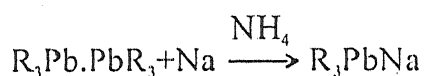
No structural information is vailable for these compounds, but they are likely to some ionic character $R_3Pb^{-8}-M^{+8}$.

Lead(II) Complexes with Schiff base :

The literature survey of last three decades reveal that very little complexes are known of lead(II) with Schiff base ligands[224-225] e.g.

Eighteen molecular adducts of PbX_2 of the type $PbX_2.L$ (where X = Cl, NO_3 and L = Schiff base ligands prepared from aromatic aldehyde or ketone (benzaldehyde, cinnamaldehyde, 2-naphthaldehyde, acctophenone with ethylenediamine) have been synthesised and characterised.[226]

Pb(II) metal complexes of Schiff base ligands of N, N'-bis (morpholinobenzyl) urea have been synthesised and characterised.[227]

Pb(II) Schiff base complexes of the type $[PbX_2L]$ (where X = Cl, Br and L = tetradentate Schiff base 1,2 glyoxilidine-bis- 2-aminoethylpyridine) have been synthesised and characterised.[228]

Pb(II) Schiff base complexes of the type $[PbX_2L]$ (where X = Cl, Br and L= Schiff base ligand of aminothiazoles) have been synthesised and characterised.[229]

[Pb(L) (SCN)$_2$] where L is the Schiff base lariat crown ether N, N'- bis (3-(salicylaldimino) benzyl-4, 13- diaza-18 crown-6) were isolated and characterised by X-ray single crystallography[230].

The macrobicyclic receptor derived from 4, 13-diaza-18-crown-6 incorporating a pyridinyl Schiff base spacer, forms stable complexes with lead(II) e.g. [Pb(L)] (ClO$_4$)$_2$.O.5H$_2$O (where L= macrobicyclic Schiff base) have been synthesised and characterised.[231]

AIM AND SCOPE OF STUDY

From a critical survey of the revelant literature of the chemitry of Pb(II) compounds, the following conclusions are evident.

Many Pb(II) compound are known but their reaction with various bidentate and tetradentate Schiff base ligands have not been studied with various PbX_2 compounds. Moreover, Pb(II) compounds have been utilised in industry.

In the light of the above facts the present investigation "Synthesis and studies on some lead(II) coordination compounds" was undertaken. During this investigation many new lead(II) compounds will be prepared and characterised by various physicochemical methods.

The chapter in this thesis have been organised to provide an easy access to the information available on the topic treated. The first two chapters deal with the general introduction of Pb(II) compounds, materials used and experiemental techniques used to characterised and synthesised compounds. In the third and fourth chapters the reaction of Pb(II) compounds with various Schiff base ligands have been discused about the synthesis and characterisation of the molecular adducts.

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CHAPTER - II

MATERIALS AND EXPERIMENTAL TECHNIQUES

This chapter deals with the source from where starting materials have been obtained. The details of analytical methods and various physicochemical techniques employed for the characterisation and elucidation of the structure of the newly synthesised complexes are also given:

Materials :

(i)   Solvent : E. Merck (L.R. Grade and Ranbaxy) solvents were used after purification and drying by conventional methods.

(ii)   Lead Chloride : (Aldrich A.R. grade) was used.

(iii) Lead bromide : (Aldrich A.R. grade) was used.

(vi)   Lead iodide : (Aldrich A.R. grade) was used.

Other starting materials used in the present investigation, prepared either from the reported methods or obtained from commercial sources as listed in table I and were used after purification.

Table - I : Specification

Sr.No.	Name	Source
1.	glyoxal	BDH
2.	2, 3- butanedione	BDH
3.	acetylacetone	Aldrich
4.	1-phenyl butane 1, 3- dione	Aldrich
5.	1,2,4,5 phenylenediamine	Aldrich
6.	2-acetylpyrrole	BDH
7.	2-pyrrole-carboxyaldehyde	BDH
8.	2-pyridyl carboxyaldehyde	Loba
9.	2-naphthylaldehyde	Loba
10.	cyclohexanediamine	Aldrich

Experimental Techniques :

The details of physicochemical techniques employed viz. melting points, conductance measurements, Infrared and X-ray photoelectron spectroscopy i.e. XPS for the characterisation and structural determination of the newly synthesised Pb (II) complexes are given below :

The melting point of the complexes were obtained on electrically operated melting point apparatus (M/s Toshniwal) and values are reported are uncorrected.

The elemental analysis for C, H and N were determined on a semimicro scale at CDRI, Lucknow.

The molar conductance of the complexes was measured at room temperature in DMF or DMSO by Digisun Electronics conductivity bridge.

The infrared spectra of the complexes and ligands were recorded on Perkin-Elmer 457 spectrometer at room temperature in KBr or CsI (for complexes) or in nujol (for ligands).

The X-ray photoelectron spectra i.e. XPS were recorded on a VG scientific ESCA -3 MK II electron spectrometer. The MgK X-ray line (1253.6 eV) was used for photoexcitation. The $Cu2p_{3/2}$ (BE= 932.8 ± 0.2) and $Au4f_{7/2}$ (BE= 83.8 ± 0.1) lines were used to

calibrate the instrument and $Ag3d_{5/2}$ (BE= 368.2) was used for cross checking[1]. All the spectra were recorded using the same spectrometer parameters of 50 eV pass energy and 4mm slit width. The reduced full width at left maximum (FWHM) at Au4f7/2 (BE=83.8 eV) level under these condition was 1.2 eV.

The powdered sample was mixed with high purity silver powder to reduce the charging effect. A thin layer of such a sample was pressed on a gold metal gauge, which was welded to a nickel sample holder. The $Ag3d_{5/2}$ level BE=368.2 eV obtained from this sample was sharp and did not show any obserable shift. Thus, the charging of the sample if at all present was negligible.[1] The spectra were recorded in triplicate in the region of interest.

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CHAPTER - III

COMPLEXES OF PbX₂ WITH TETRADENTATE SCHIFF BASE LINGANDS

A literature survey reveals that many Pb (II) compounds have been reported but Pb (II) compounds with Schiff base and macrocyclic Schiff base ligands are less known.[1-2]

This chapter deals with the interaction of Pb (II) halides i.e. $PbCl_2$, $PbBr_2$, PbI_2 with various tetradentate macrocyclic Schiff base ligands in various molar ratio. The product which will be obtained, will be characterised by various physicochemical methods to establish structure and geometry.

EXPERIMENTAL

The $PbCl_2$, $PbBr_2$ and PbI_2 are used from Aldrich.

Preparation of Schiff base ligands :

In 2 mmol of glyoxal or 2, 3- butanedione or acetylacetone or 1- phenyl butane-1, 3 dione in dry methanol (50 ml) was mixed 1 mmol 1, 2, 4, 5 phenylenediamine and was refluxed for 3-4 hrs. The solid product was obtained, filtered washed with dry methanol and air-dried.

Thus, the following four macrocyclic Schiff base complexes were prepared :

(1)

glyoxal   1, 2, 4, 5 phenylenediamine

bis (glyoxal) 1, 2, 4, 5 phenylenediamine

L^1

(2)

2,3- butanedione

bis (2,3- butanedione) 1, 2, 4, 5 phenylenediamine

L^2

(3)

acetylacetone

bis (acetylaetone) 1, 2, 4, 5 phenylenediamine

L^3

(4)

1-phenylbutance-1, 3- dione

bis (1- phenybutane-1, 3-dione) 1, 2, 4; 5 phenylenediamine

L^4
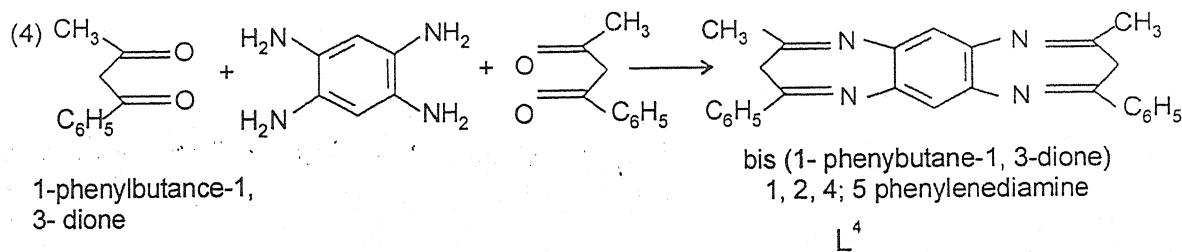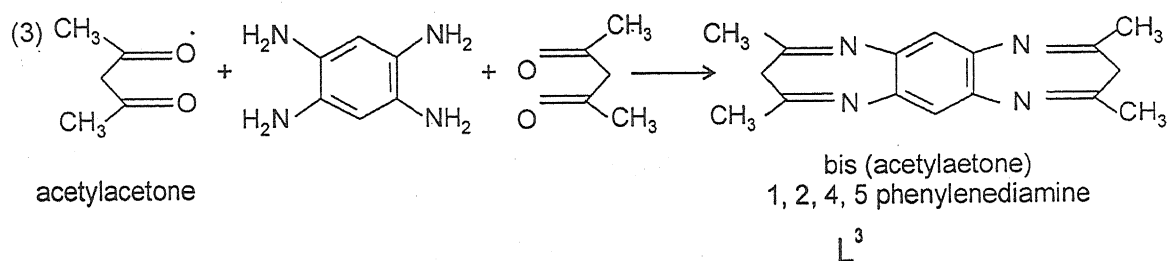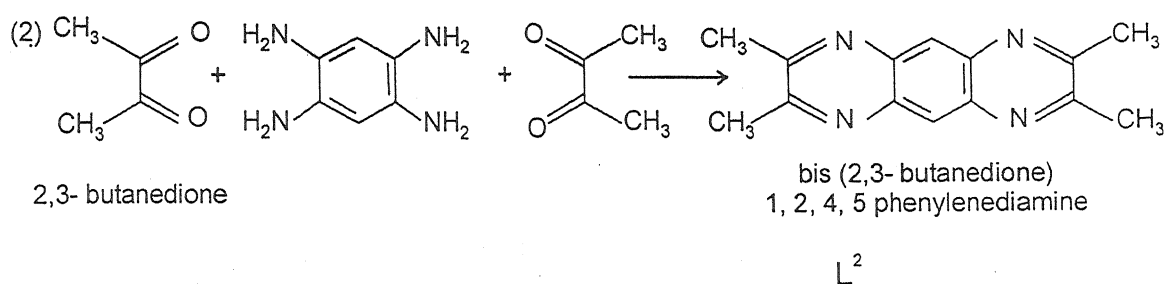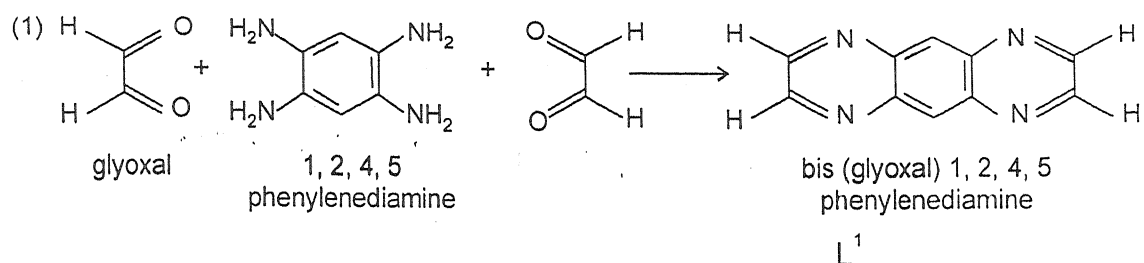
Preparation of [PbX$_2$. L] complexes :

1mmol PbX$_2$ (X = Cl or Br or I) in 50ml dry methanol was mixed with 1mmol of any above prepared macrocyclic Schiff base (L^1 or L^2 or L^3 or L^4) and entire mixture was refluxed for 3-4 hrs. The soild product was obtained, filtered, washed with dry methanol and air-dried.

Preparation of [(PbX$_2$)$_2$. L] complexes :

2mmol PbX$_2$ (X = Cl or Br or I) in 50ml dry methanol was mixed with 1mmol of any above prepared macrocyclic chiff base ligand (L^1 or L^2 or L^3 or L^4) and entire the mixture was refluxed for 3-4 hrs. The soild product was obtained, filtered, washed with methanol and air-dried.

Preparation of [(PbX$_2$)$_3$. L] complexes :

3mmol of SnX$_2$ (X = Cl or Br or I) in 50ml dry methanol was mixed 1mmol of any above prepared macrocyclic Schiff base ligand (L^1 or L^2 or L^3 or L^4) and entire mixture was refluxed for 3-4 hrs. The soild product was obtained, filtered, washed with dry methanol and air-dried.

Preparation of [(PbX$_2$)$_4$. L] complexes :

4mmol PbX$_2$ (X = Cl or Br or I) in 50ml dry methonl was mixed 1mmol of any above prepared macrocyclic Schiff base ligand

(L^1 or L^2 or L^3 or L^4) and entire mixture was refluxed for 3-4 hrs. The soild product was obtained, filtered, washed with methanol and air-dried.

RESULTS AND DISCUSSION :

The new molecular adducts have been synthesised by the interaction of PbX_2 with any prepared above macrocyclic Schiff base legands :

$$PbX_2 + L \longrightarrow [PbX_2 . L]$$
$$(X = Cl \text{ or } Br \text{ or } I)$$
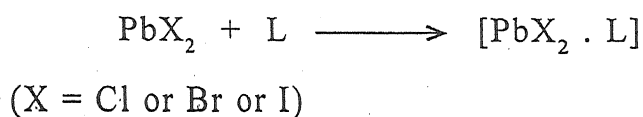
All these prepared molecular adducts are white in colour. They all are stable towards the atmospheric oxygen and moisture. They all are stable at room temperature even for a longer time.

The elemental analysis and molar conductance of all these prepared compounds are listed in Table- I. Molar conductance of $10^{-3}M$ solution of the complexes were determined at room temperature. The values ranges from 20-30 ohm^{-1} cm^2 mol^{-1} in DMF suggesting nonelectrotyte nature of all these complexes.[3]

In these molecular adducts, the $\rangle c = N$ modes undergo shift to higher wave numbers i.e. $\rangle c=N$ in the ligand, 1610-1620 cm^{-1} and $\rangle c = N$ in molecular adducts 1635 - 1670 cm^{-1}, suggesting the coordination from nitrogen atom of the ligands[4-5]. Infrared

frequency associated with fundamental modes of vibration of γPb-N and γPb-X was observed in the range 305-330 cm^{-1} and 280-285 cm^{-1} respectively.[6]

The binding energies (eV) of PbX_2 and their prepared molecular adducts $[PbX_2.L]$; $[(PbX_2)_2.L]$; $[(PbX_2)_3.L]$ and $[(PbX_2)_4.L]$ for Pb2p and N1s photoelectron peaks are listed in table 2. It was observed that the binding energies of Pb2p in the starting material PbX_2 was higher than in the prepared molecular adducts $[PbX_2.L]$; $[(PbX_2)_2.L]$; $[(PbX_2)_3.L]$ and$[(PbX_2)_4.L]$. These observation suggest that the electron density of Pb(II) metal ion has increased due to coordination of ligands with Pb(II) metal ion[7].(table 2-4 and fig 1-3) Moreover, the values of N1s binding energy (eV) in $[PbX_2.L]$; $[(PbX_2)_2.L]$; $[(PbX_2)_3.L]$ and$[(PbX_2)_4.L]$ molecular adducts have been observed increased than free ligands (table 5-8 and fig 4-7). This also concluded coordination of nitrogen atom with metal ion of PbX_2[7].

On the basis of elemental analysis, molar conductance data showing that all these molecular adducts are nonionic and IR and X-ray photoelectron spectra (XPS) results showing the side of coordination, it is possible to assign a structure for each adduct as shown in figs 8-55.All these molecular adducts are having sp^3 on

hybridisation i.e. tetrahedral geometry as show below:
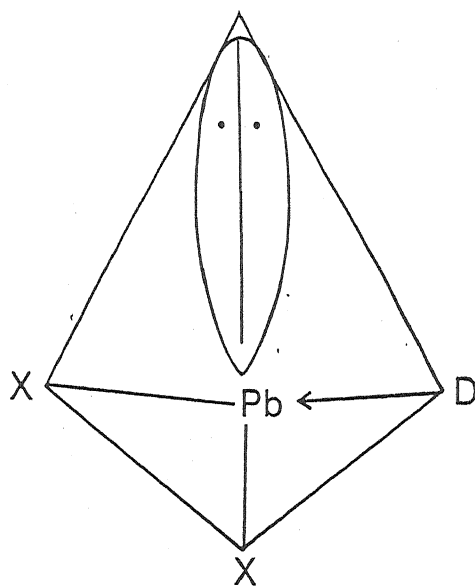
Structure of $[(PbX_2)_x.D]$

Table- I : Analytical data of [PbX$_2$.L]; [(PbX$_2$)$_2$.L]; [(PbX$_2$)$_3$.L] and[(PbX$_2$)$_4$.L] compounds.

S.No.	Compound	% Found (Calculated)			Molar conductance in DMF OHM^{-1} CM^2 MOL^{-1}
		C	H	N	
1.	[Pb Cl$_2$.L^1]	26.2 (26.0)	1.3 (1.3)	12.0 (12.0)	20
2.	[Pb Br$_2$.L^1]	21.4 (21.8)	1.0 (1.0)	10.0 (10.1)	22
3.	[Pb I$_2$.L^1]	18.4 (18.6)	0.9 (0.9)	8.6 (8.7)	24
4.	[(Pb Cl$_2$)$_2$.L^1]	16.2 (16.3)	0.8 (0.8)	7.4 (7.4)	16
5.	[(Pb Br$_2$)$_2$.L^1]	13.2 (13.0)	0.6 (0.6)	6.0 (6.1)	18
6.	[(Pb I$_2$)$_2$.L^1]	10.4 (10.8)	0.5 (0.5)	5.0 (5.0)	16
7.	[(Pb Cl$_2$)$_3$.L^1]	12.4 (12.6)	0.5 (0.5)	5.2 (5.5)	20
8.	[(Pb Br$_2$)$_3$.L^1]	9.2 (9.3)	0.4 (0.4)	4.0 (4.3)	18
9.	[(Pb I$_2$)$_3$.L^1]	7.8 (7.6)	0.3 (0.3)	3.4 (3.5)	16
10.	[(Pb Cl$_2$)$_4$.L^1]	9.4 (9.2)	0.4 (0.4)	4.2 (4.3)	12
11.	[(Pb Br$_2$)$_4$.L^1]	7.2 (7.2)	0.3 (0.3)	3.2 (3.3)	10

S.No.	Compound	% Found (Calculated)			Molar conductance in DMF OHM^{-1} CM^2 MOL^{-1}
		C	H	N	
12.	$[(Pb\ I_2)_4.L^1]$	5.8 (5.9)	0.2 (0.2)	2.6 (2.7)	18
13.	$[(Pb\ Cl_2).L^2]$	35.0 (35.2)	3.3 (3.3)	10.0 (10.2)	18
14.	$[(Pb\ Br_2).L^2]$	30.2 (30.3)	2.4 (2.8)	8.6 (8.8)	20
15.	$[(Pb\ I_2).L^2]$	26.2 (26.4)	2.2 (2.4)	7.6 (7.7)	22
16.	$[(Pb\ Cl_2)_2.L^2]$	23.2 (23.3)	2.0 (2.1)	6.4 (6.8)	24
17.	$[(Pb\ Br_2)_2.L^2]$	19.0 (19.1)	1.6 (1.7)	5.6 (5.5)	22
18.	$[(Pb\ I_2)_2.L^2]$	16.0 (16.1)	1.4 (1.5)	4.6 (4.7)	20
19.	$[(Pb\ Cl_2)_3.L^2]$	17.2 (17.4)	1.6 (1.6)	5.0 (5.0)	12
20.	$[(Pb\ Br_2)_3.L^2]$	14.0 (14.0)	1.2 (1.3)	4.0 (4.0)	10
21.	$[(Pb\ I_2)_3.L^2]$	11.4 (11.6)	1.0 (1.0)	3.2 (3.3)	12
22.	$[(Pb\ Cl_2)_4.L^2]$	13.8 (13.9)	1.2 (1.3)	4.0 (4.0)	10
23.	$[(Pb\ Br_2)_4.L^2]$	11.0 (11.0)	1.0 (1.0)	3.0 (3.2)	12

S.No.	Compound	% Found (Calculated)			Molar conductance in DMF OHM^{-1} CM^2 MOL^{-1}
		C	H	N	
24.	$[(Pb\ I_2)_4.L^2]$	9.0 (9.0)	0.8 (0.8)	2.4 (2.6)	10
25.	$[(Pb\ Cl_2).L^3]$	32.4 (32.5)	2.7 (2.7)	10.6 (10.8)	18
26.	$[(Pb\ Br_2).L^3]$	27.6 (27.7)	2.0 (2.3)	9.0 (9.2)	20
27.	$[(Pb\ I_2).L^3]$	24.0 (24.0)	2.2 (2.2)	8.0 (8.0)	22
28.	$[(Pb\ Cl_2)_2.L^3]$	2.0 (2.1)	1.7 (1.7)	7.2 (7.0)	24
29.	$[(Pb\ Br_2)_2.L^3]$	17.0 (17.2)	1.4 (1.4)	5.6 (5.7)	10
30.	$[(Pb\ I_2)_2.L^3]$	14.0 (14.4)	1.2 (1.2)	4.6 (4.8)	12
31.	$[(Pb\ Cl_2)_3.L^3]$	15.4 (15.6)	1.3 (1.3)	5.0 (5.2)	10
32.	$[(Pb\ Br_2)_3.L^3]$	12.4 (12.5)	1.0 (1.0)	4.0 (4.1)	14
33.	$[(Pb\ I_2)_3.L^3]$	10.2 (10.3)	0.8 (0.8)	3.2 (3.4)	16
34.	$[(Pb\ Cl_2)_4.L^3]$	12.2 (12.4)	1.0 (1.0)	4.0 (4.1)	20
35.	$[(Pb\ Br_2)_4.L^3]$	9.8 (9.8)	0.8 (0.8)	3.0 (3.2)	22

S.No.	Compound	% Found (Calculated)			Molar conductance in DMF OHM^{-1} CM^2 MOL^{-1}
		C	H	N	
36.	$[(Pb\ I_2)_4.L^3]$	8.0 (8.0)	0.6 (0.6)	2.4 (2.6)	18
37.	$[(Pb\ Cl_2).L^4]$	46.6 (46.6)	3.0 (3.2)	8.2 (8.3)	10
38.	$[(Pb\ Br_2).L^4]$	41.0 (41.2)	2.8 (2.9)	7.2 (7.3)	12
39.	$[(Pb\ I_2).L^4]$	36.0 (36.6)	2.5 (2.5)	6.4 (6.5)	14
40.	$[(Pb\ Cl_2)_2.L^4]$	32.8 (32.9)	2.3 (2.3)	5.8 (5.9)	16
41.	$[(Pb\ Br_2)_2.L^4]$	27.6 (27.7)	1.9 (1.9)	4.8 (4.9)	20
42.	$[(Pb\ I_2)_2.L^4]$	23.6 (23.7)	1.6 (1.6)	4.0 (4.2)	22
43.	$[(Pb\ I_2)_3.L^4]$	25.2 (25.4)	1.7 (1.7)	4.0 (4.5)	20
44.	$[(Pb\ Br_2)_3.L^4]$	20.8 (20.9)	1.4 (1.4)	3.6 (3.7)	24
45.	$[(Pb\ I_2)_3.L^4]$	17.4 (17.5)	1.2 (1.2)	3.0 (3.1)	20
46.	$[(Pb\ Cl_2)_4.L^4]$	20.6 (20.7)	1.4 (1.4)	3.8 (3.7)	18
47.	$[(Pb\ Br_2)_4.L^4]$	16.6 (16.7)	1.1 (1.1)	3.1 (3.0)	16
48.	$[(Pb\ I_2)_4.L^4]$	13.8 (13.9)	0.9 (0.9)	2.6 (2.5)	18

Table- 2 : Pb2p binding energies (eV) in $PbCl_2$ and $[PbCl_2)_X.L]$ compounds.

S.No.	Compound	Pb2p
1.	$PbCl_2$	764.8
2.	$[PbCl_2.L^1]$	763.6
3.	$[(PbCl_2)_2.L^1]$	763.6
4.	$[(PbCl_2)_3.L^1]$	763.6
5.	$[(PbCl_2)_4.L^1]$	763.6
6.	$[(PbCl_2).L^2]$	763.6
7.	$[(PbCl_2)_2.L^2]$	763.6
8.	$[(PbCl_2)_3.L^2]$	763.6
9.	$[(PbCl_2)_4.L^2]$	763.6
10.	$[(PbCl_2).L^3]$	763.6
11.	$[(PbCl_2)_2.L^3]$	763.6
12.	$[(PbCl_2)_3.L^3]$	763.6
13.	$[(PbCl_2)_4.L^3]$	763.6
14.	$[(PbCl_2).L^4]$	763.6
15.	$[(PbCl_2)_2.L^4]$	763.6
16.	$[(PbCl_2)_3.L^4]$	763.6
17.	$[(PbCl_2)_4.L^4]$	763.6

Table- 3 : Pb2p binding energies (eV) in $PbBr_2$ and $[PbBr_2)_x.L]$ compounds.

S.No.	Compound	Pb2p
1.	$PbBr_2$	764.6
2.	$[(PbBr_2).L^1]$	763.4
3.	$[(PbBr_2)_2.L^1]$	763.4
4.	$[(PbBr_2)_3.L^1]$	763.4
5.	$[(PbBr_2)_4.L^1]$	763.4
6.	$[(PbBr_2).L^2]$	763.4
7.	$[(PbBr_2)_2.L^2]$	763.4
8.	$[(PbBr_2)_3.L^2]$	763.4
9.	$[(PbBr_2)_4.L^2]$	763.4
10.	$[(PbBr_2).L^3]$	763.4
11.	$[(PbBr_2)_2.L^3]$	763.4
12.	$[(PbBr_2)_3.L^3]$	763.4
13.	$[(PbBr_2)_4.L^3]$	763.4
14.	$[(PbBr_2).L^4]$	763.4
15.	$[(PbBr_2)_2.L^4]$	763.4
16.	$[(PbBr_2)_3.L^4]$	763.4
17.	$[(PbBr_2)_4.L^4]$	763.4

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Table- 4 : Pb2p binding energies (eV) in PbI_2 and $[PbI_2)_X.L]$ compounds.

S.No.	Compound	Pb2p
1.	PbI_2	764.4
2.	$[(PbI_2).L^1]$	763.2
3.	$[(PbI_2)_2.L^1]$	763.2
4.	$[(PbI_2)_3.L^1]$	763.2
5.	$[(PbI_2)_4.L^1]$	763.2
6.	$[(PbI_2).L^2]$	763.2
7.	$[(PbI_2)_2.L^2]$	763.2
8.	$[(PbI_2)_3.L^2]$	763.2
9.	$[(PbI_2)_4.L^2]$	763.2
10.	$[(PbI_2).L^3]$	763.2
11.	$[(PbI_2)_2.L^3]$	763.2
12.	$[(PbI_2)_3.L^3]$	763.2
13.	$[(PbI_2)_4.L^3]$	763.2
14.	$[(PbI_2).L^4]$	763.2
15.	$[(PbI_2)_2.L^4]$	763.2
16.	$[(PbI_2)_3.L^4]$	763.2
17.	$[(PbI_2)_4.L^4]$	763.2

Table- 5 : N1s binding energies (eV) in L^1 and $[PbX_2)_x.L^1]$

S.No.	Ligand & compound	N1s	
		Ligand or uncoord	Coord
1.	Ligand L^1	400.6	-
2.	$[(PbCl_2).L^1]$	400.6	403.8
3.	$[(PbBr_2).L^1]$	400.6	403.8
4.	$[(PbI_2).L^1]$	400.6	403.8
5.	$[(PbCl_2)_2.L^1]$	400.6	403.8
6.	$[(PbBr_2)_2.L^1]$	400.6	403.8
7.	$[(PbI_2)_2.L^1]$	400.6	403.8
8.	$[(PbCl_2)_3.L^1]$	400.6	403.8
9.	$[(PbBr_2)_3.L^1]$	400.6	403.8
10.	$[(PbI_2)_3.L^1]$	400.6	403.8
11.	$[(PbCl_2)_4.L^1]$	-	403.8
12.	$[(PbBr_2)_4.L^1]$	-	403.8
13.	$[(PbI_2)_4.L^1]$	-	403.8

Table- 6 : N1s binding energies (eV) in L^2 and $[PbX_2)_X.L^2]$

S.No.	Ligand & compound	N1s	
		Ligand or uncoord	Coord
1.	Ligand L^2	400.8	-
2.	$[(PbCl_2).L^2]$	400.8	403.8
3.	$[(PbBr_2).L^2]$	400.8	403.8
4.	$[(PbI_2).L^2]$	400.8	403.8
5.	$[(PbCl_2)_2.L^2]$	400.8	403.8
6.	$[(PbBr_2)_2.L^2]$	400.8	403.8
7.	$[(PbI_2)_2.L^2]$	400.8	403.8
8.	$[(PbCl_2)_3.L^2]$	400.8	403.8
9.	$[(PbBr_2)_3.L^2]$	400.8	403.8
10.	$[(PbI_2)_3.L^2]$	400.8	403.8
11.	$[(PbCl_2)_4.L^2]$	-	403.8
12.	$[(PbBr_2)_4.L^2]$	-	403.8
13.	$[(PbI_2)_4.L^2]$	-	403.8

Table- 7 : N1s binding energies (eV) in L^3 and $[PbX_2)_x.L^3]$

S.No.	Ligand & compound	N1s	
		Ligand or uncoord	Coord
1.	Ligand L^3	400.8	403.8
2.	$[(PbCl_2).L^3]$	400.8	403.8
3.	$[(PbBr_2).L^3]$	400.8	403.8
4.	$[(PbI_2).L^3]$	400.8	403.8
5.	$[(PbCl_2)_2.L^3]$	400.8	403.8
6.	$[(PbBr_2)_2.L^3]$	400.8	403.8
7.	$[(PbI_2)_2.L^3]$	400.8	403.8
8.	$[(PbCl_2)_3.L^3]$	400.8	403.8
9.	$[(PbBr_2)_3.L^3]$	400.8	403.8
10.	$[(PbI_2)_3.L^3]$	400.8	403.8
11.	$[(PbCl_2)_4.L^3]$	-	403.8
12.	$[(PbBr_2)_4.L^3]$	-	403.8
13.	$[(PbI_2)_4.L^3]$	-	403.8

Table- 8 : N1s binding energies (eV) in L^4 and $[PbX_2)_x.L^4]$

S.No.	Ligand & compound	N1s Ligand or uncoord	Coord
1.	Ligand L^4	400.8	-
2.	$[(PbCl_2).L^4]$	400.8	404.4
3.	$[(PbBr_2).L^4]$	400.8	404.4
4.	$[(PbI_2).L^4]$	400.8	404.4
5.	$[(PbCl_2)_2.L^4]$	400.8	404.4
6.	$[(PbBr_2)_2.L^4]$	400.8	404.4
7.	$[(PbI_2)_2.L^4]$	400.8	404.4
8.	$[(PbCl_2)_3.L^4]$	400.8	404.4
9.	$[(PbBr_2)_3.L^4]$	400.8	404.4
10.	$[(PbI_2)_3.L^4]$	400.8	404.4
11.	$[(PbCl_2)_4.L^4]$	-	404.4
12.	$[(PbBr_2)_4.L^4]$	-	404
13.	$[(PbI_2)_4.L^4]$	-	404

Pb2p photoelectron peak

Fig.1 : Pb2p binding energies (eV) in $PbCl_2$ and $[(PbCl_2)_x.L]$ Compounds.

Pb2p photoelectron peak
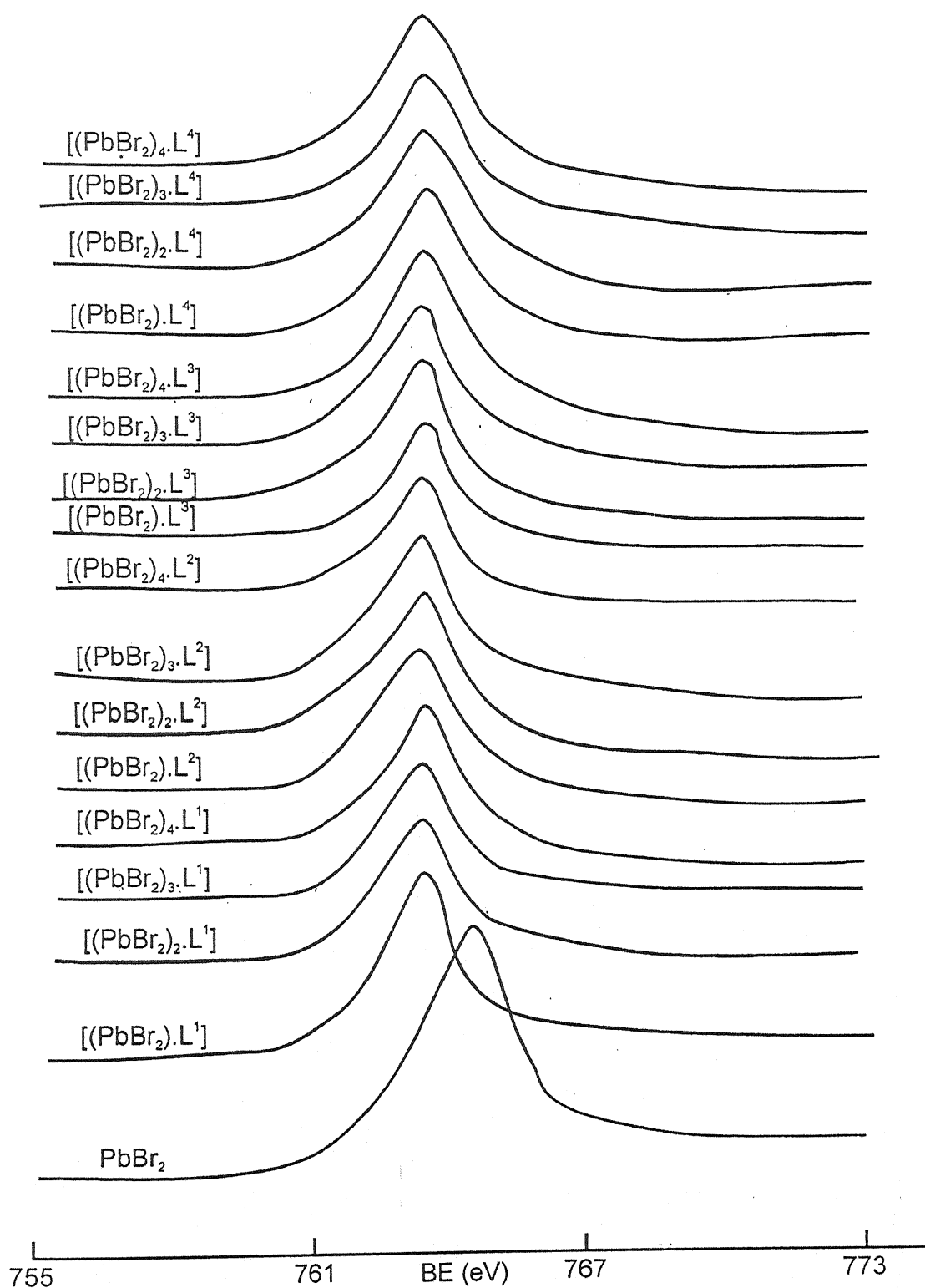
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[(PbBr$_2$)$_4$.L^4]
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[(PbBr$_2$)$_4$.L^3]
[(PbBr$_2$)$_3$.L^3]
[(PbBr$_2$)$_2$.L^3]
[(PbBr$_2$).L^3]
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[(PbBr$_2$)$_3$.L^1]
[(PbBr$_2$)$_2$.L^1]
[(PbBr$_2$).L^1]
PbBr$_2$

755   761   BE (eV)   767   773

Fig.2 : Pb2p binding energies (eV) in PbBr$_2$ and [(PbBr$_2$)$_x$.L] Complexes.

104

Pb2p photoelectron peak

$[(PbI_2)_4.L^4]$

$[(PbI_2)_3.L^4]$

$[(PbI_2)_2.L^4]$

$[(PbI_2).L^4]$

$[(PbI_2)_4.L^3]$

$[(PbI_2)_3.L^3]$

$[(PbI_2)_2.L^3]$

$[(PbI_2).L^3]$

$[(PbI_2)_4.L^2]$

$[(PbI_2)_3.L^2]$

$[(PbI_2)_2.L^2]$

$[(PbI_2).L^2]$

$[(PbI_2)_4.L^1]$

$[(PbI_2)_3.L^1]$

$[(PbI_2)_2.L^1]$

$[(PbI_2).L^1]$

PbI_2

755   761   BE (eV)   767   773
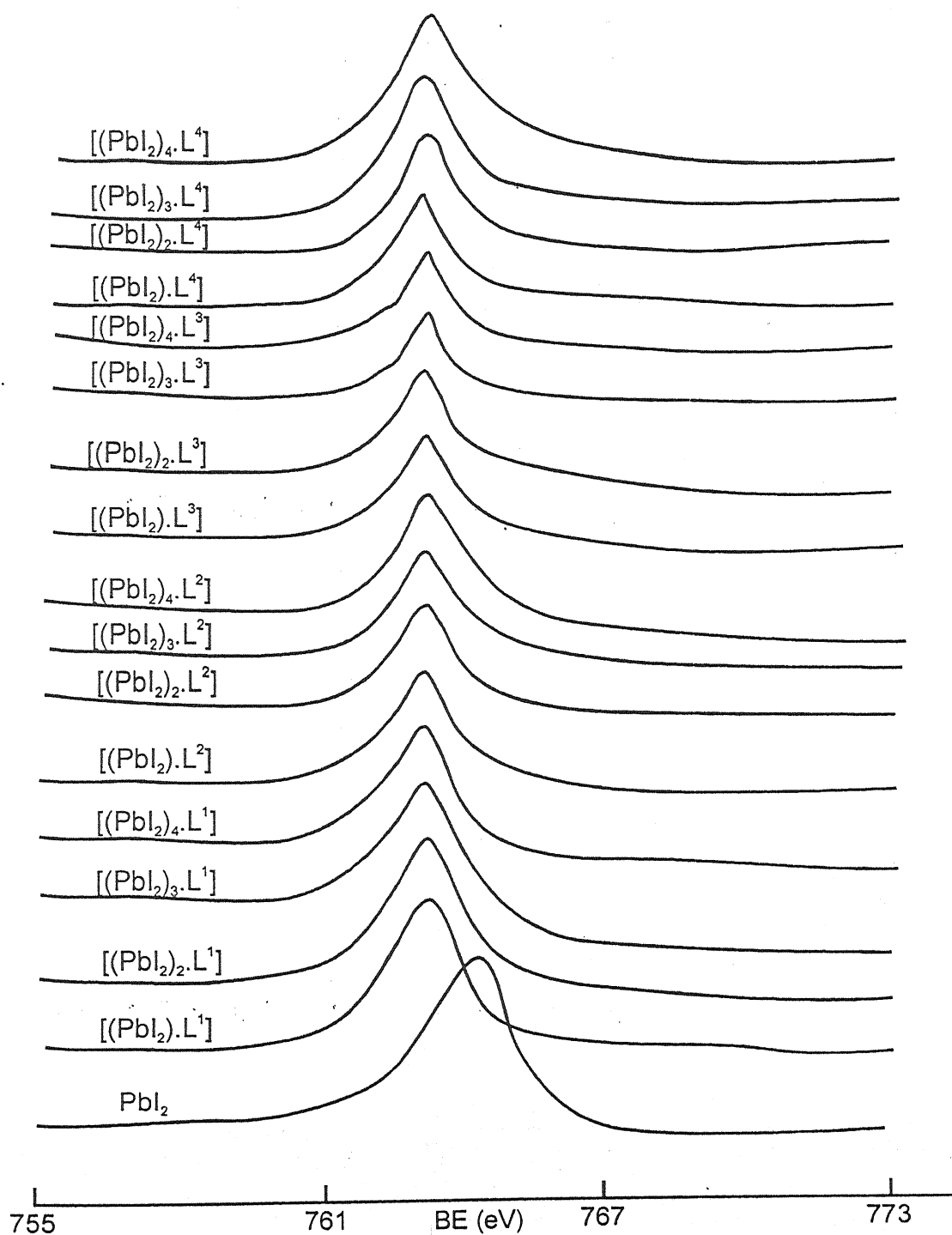
Fig.3 : Pb2p binding energies (eV) in PbI_2 and $[(PbI_2)_x.L]$ Complexes.

N1s photoelectron peak

$[(PbBr_2)_4.L^1]$

$[(PbBr_2)_3.L^1]$

$[(PbBr_2)_2.L^1]$

$[PbBr_2.L^1]$

$[(PbCl_2)_4.L^1]$

$[(PbCl_2)_3.L^1]$

$[(PbCl_2)_2.L^1]$

$[PbCl_2.L^1]$

Ligand L^1

390   396   BE (eV)   402   408
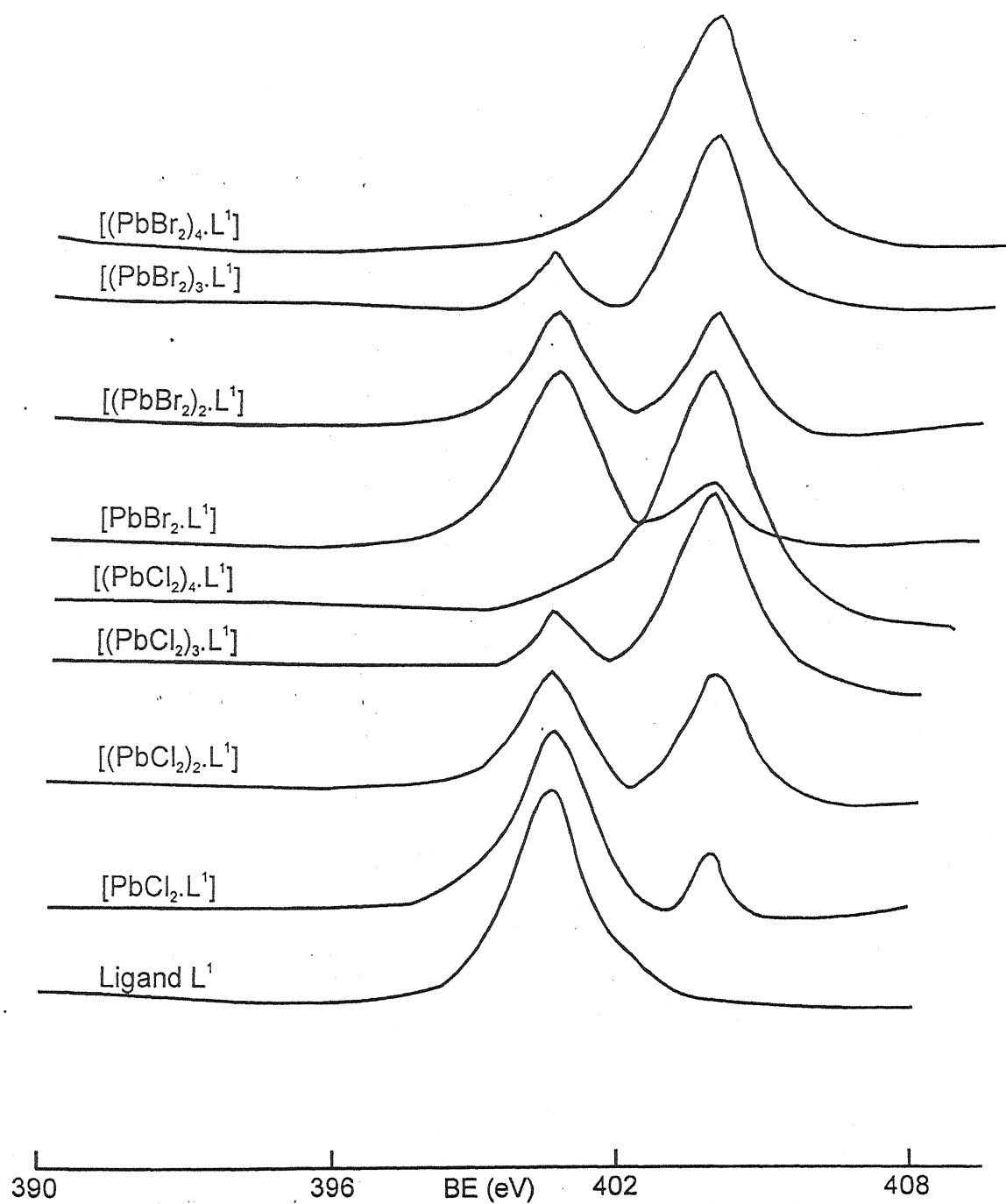
Fig.4 : N1s binding energies (eV) in L^1 and $[(PbX_2)_x.L^1]$ Complexes.

106

N1s photoelectron peak

$[(PbI_2)_4.L^4]$

$[(PbI_2)_3.L^4]$

$[(PbI_2)_2.L^4]$

$[(PbI_2).L^4]$

$[(PbCl_2)_4.L^1]$

$[(PbCl_2)_3.L^1]$

$[(PbCl_2)_2.L^1]$

$[PbCl_2.L^1]$

Ligand L^1

390   396   BE (eV)   402   408
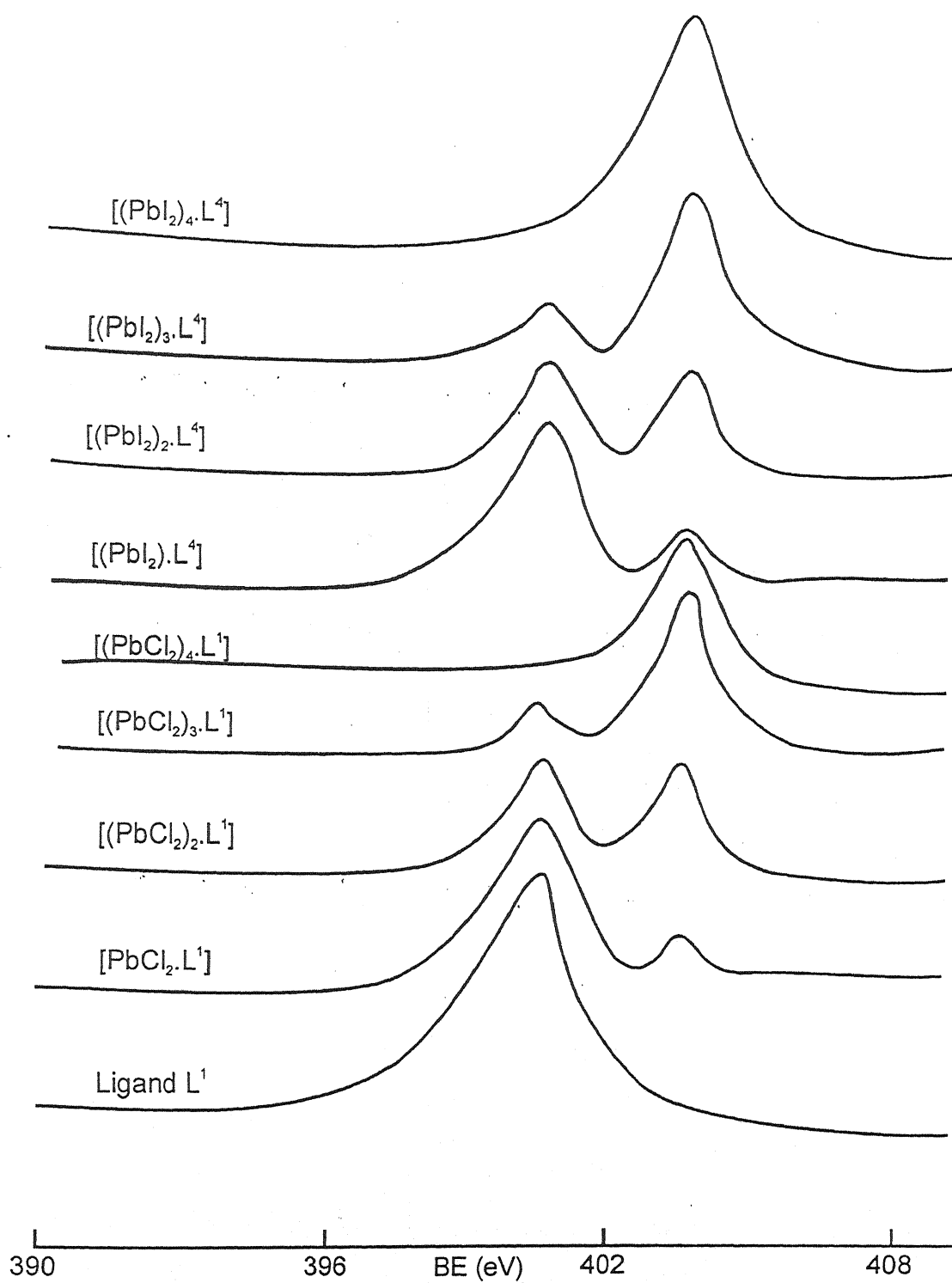
Fig.5 : N1s binding energies (eV) in L^2 and $[(PbX_2)_x.L^2]$ Complexes.

N1s photoelectron peak

$[(PbI_2)_4.L^3]$

$[(PbI_2)_3.L^3]$

$[(PbI_2)_2.L^3]$

$[PbI_2.L^3]$

$[(PbCl_2)_4.L^3]$

$[(PbCl_2)_3.L^3]$

$[(PbCl_2)_2.L^3]$

$[PbCl_2.L^3]$

Ligand L^3

390   396   BE (eV)   402   408

Fig.6 : N1s binding energies (eV) in L^3 and $[(PbX_2)_x.L^3]$ Complexes.

N1s photoelectron peak

Fig.7 : N1s binding energies (eV) in L^4 and $[(PbX_2)_x.L^4]$ Complexes.

Fig. 8

Fig. 9

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Fig. 10

Fig. 11

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Fig. 12

Fig. 13

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Fig. 14

Fig. 15

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Fig. 16

Fig. 17

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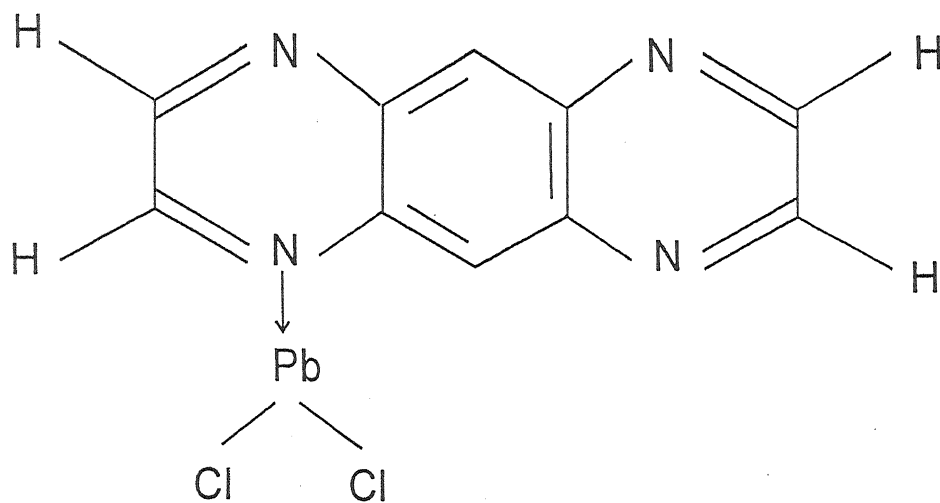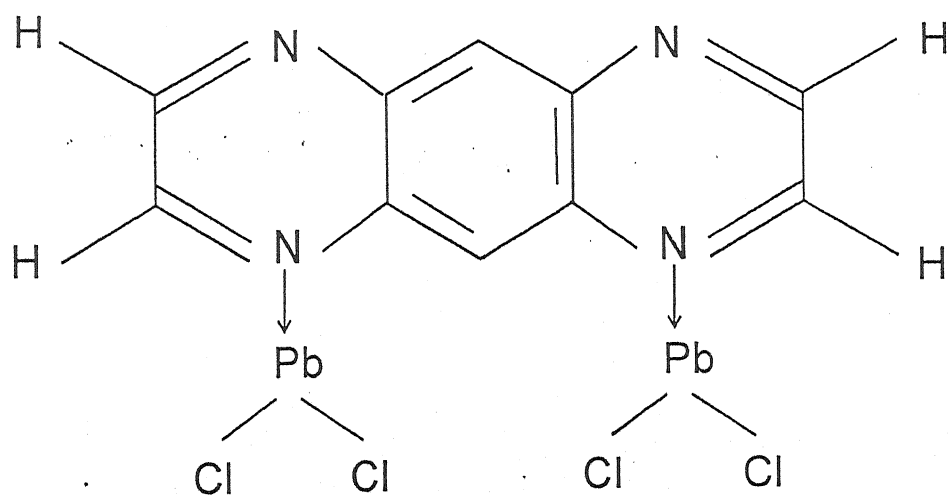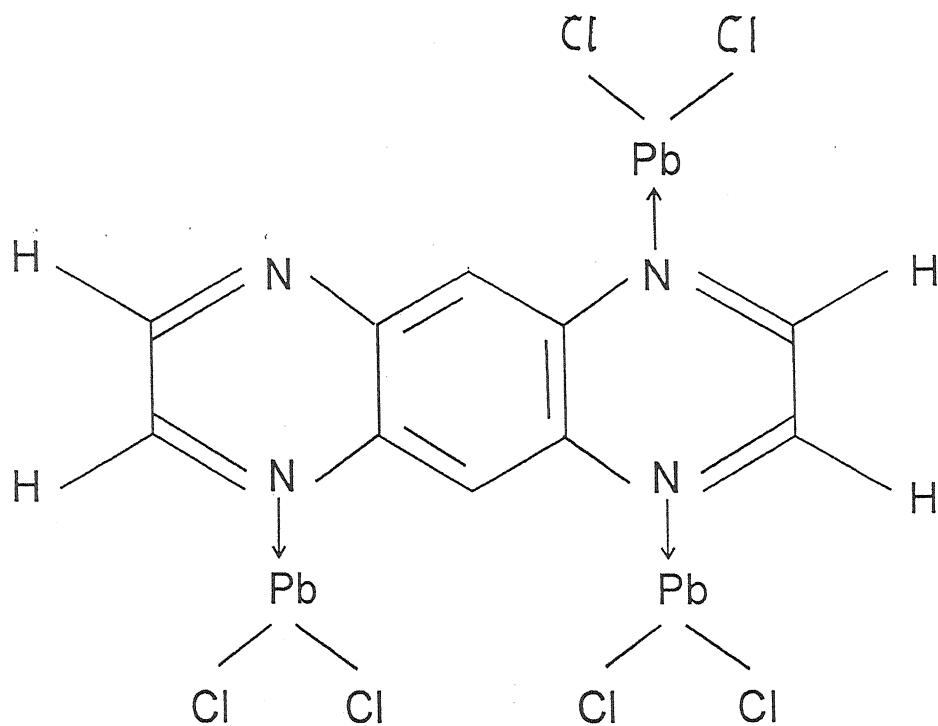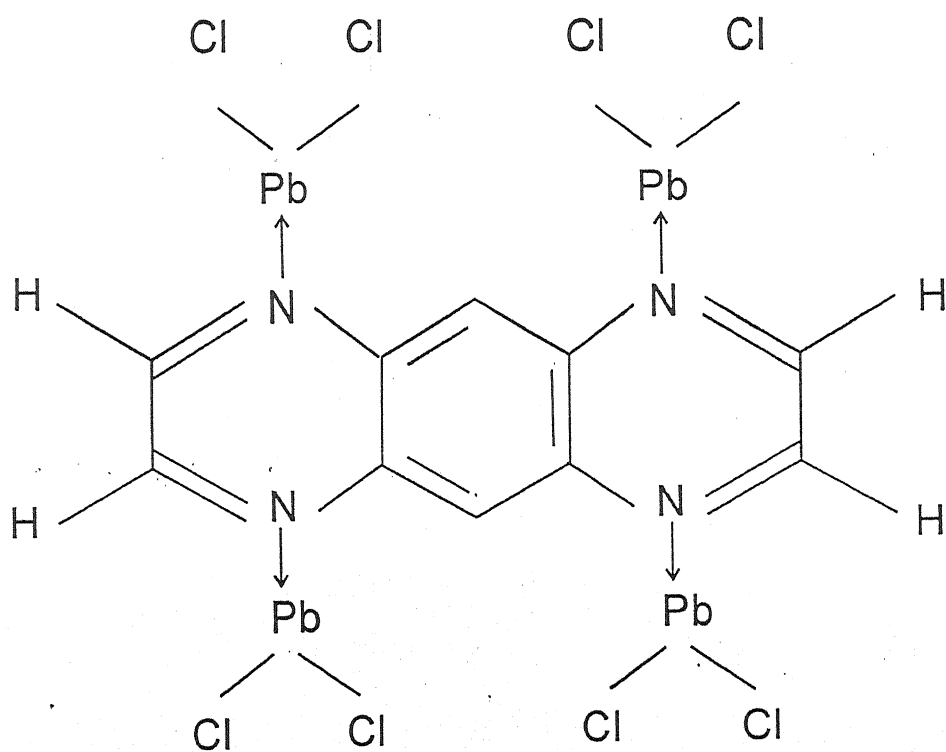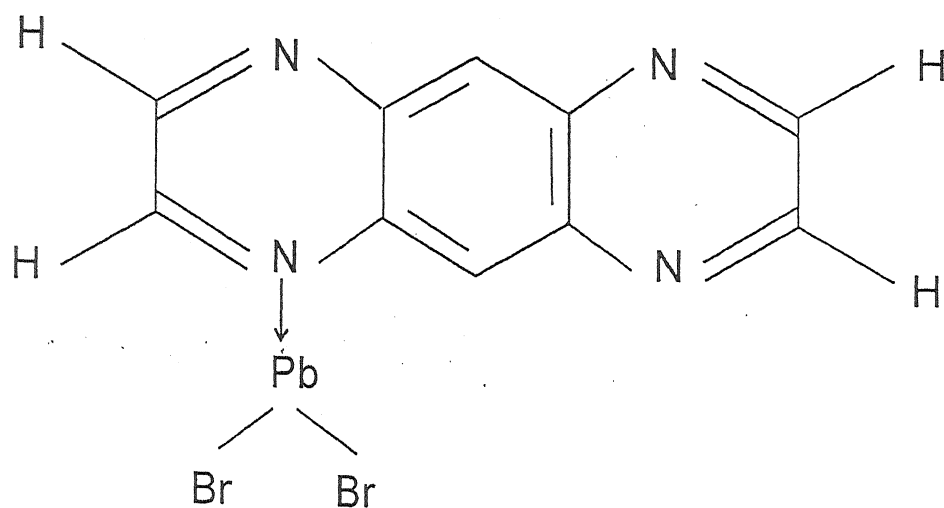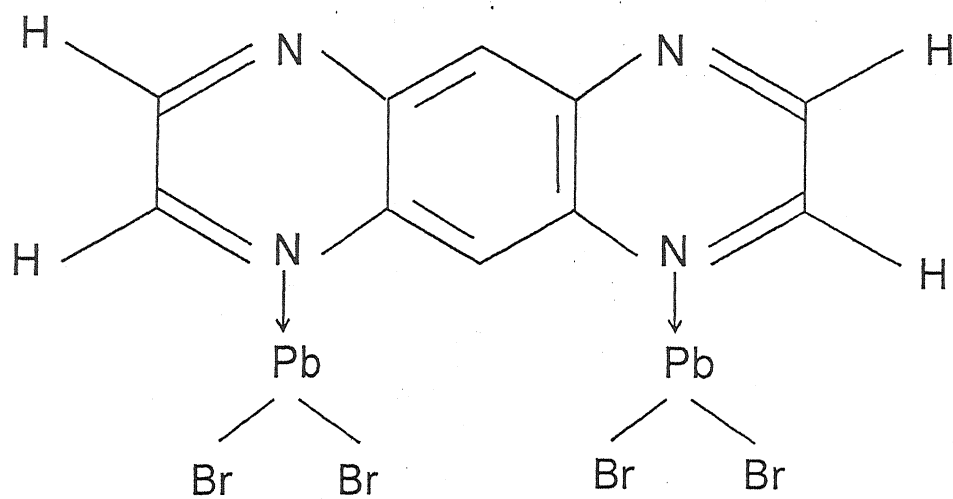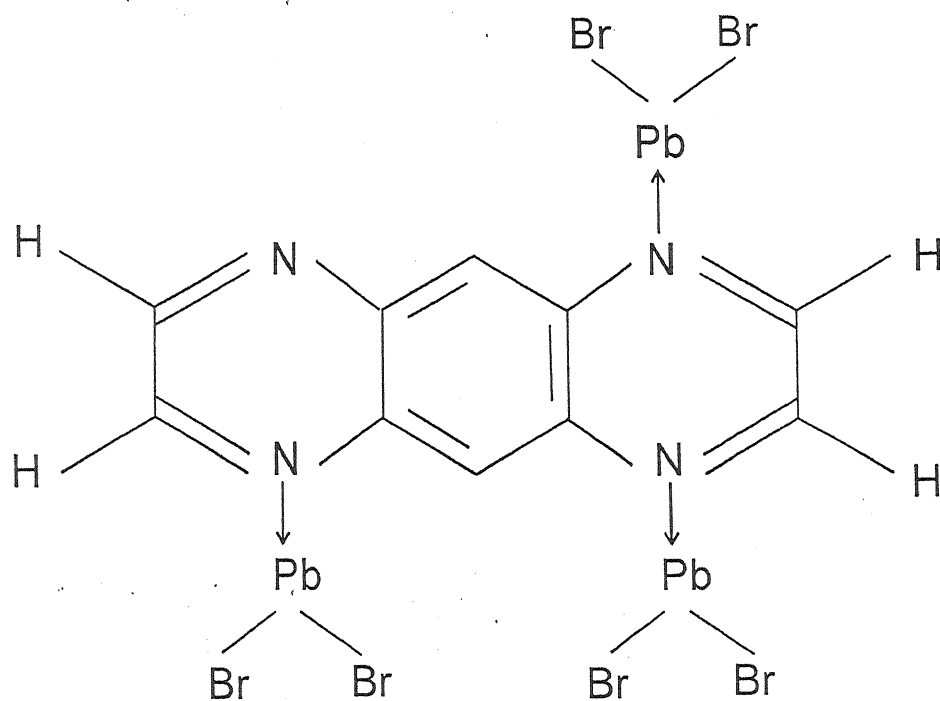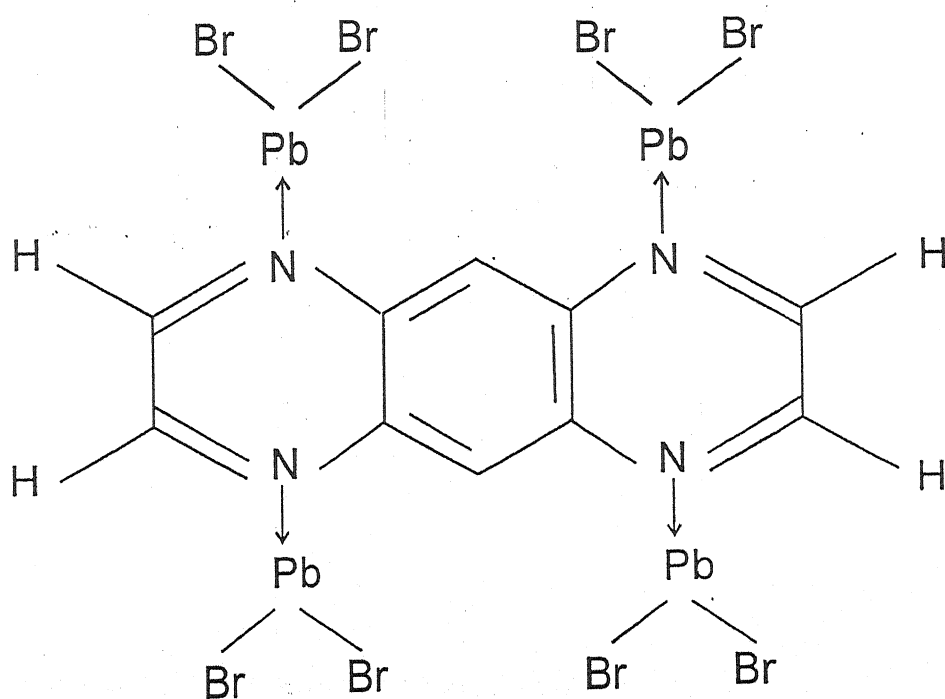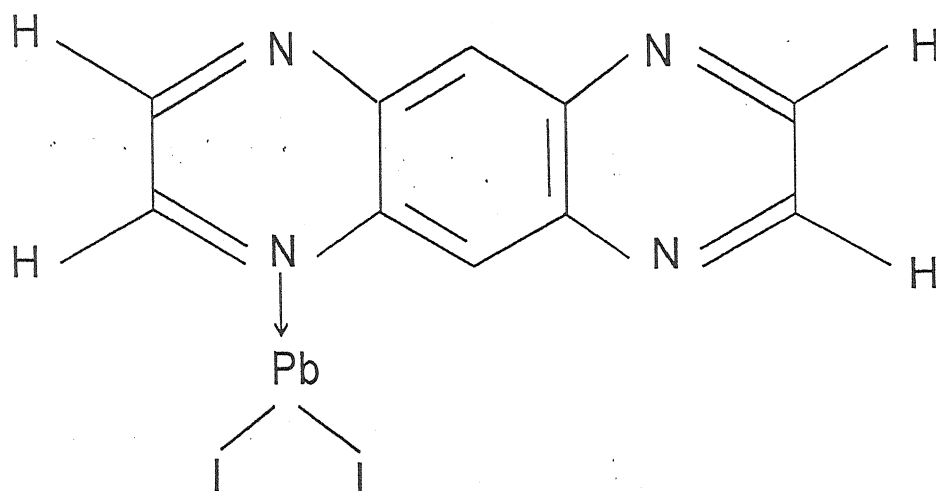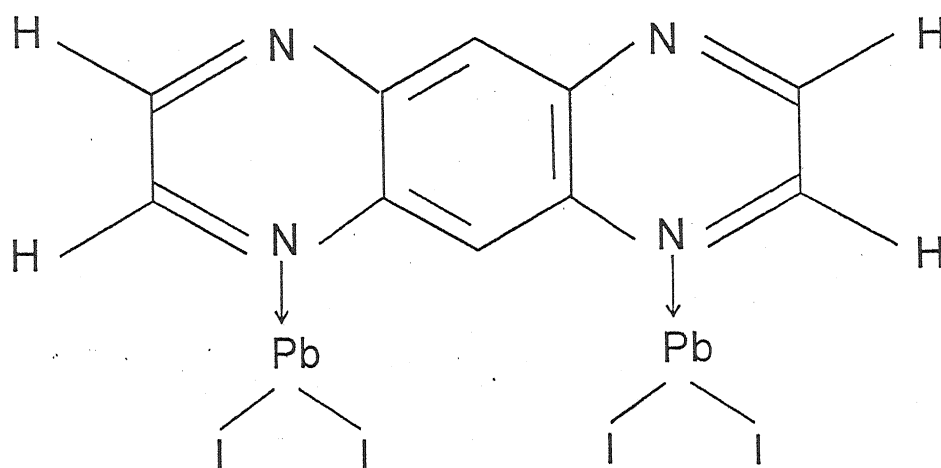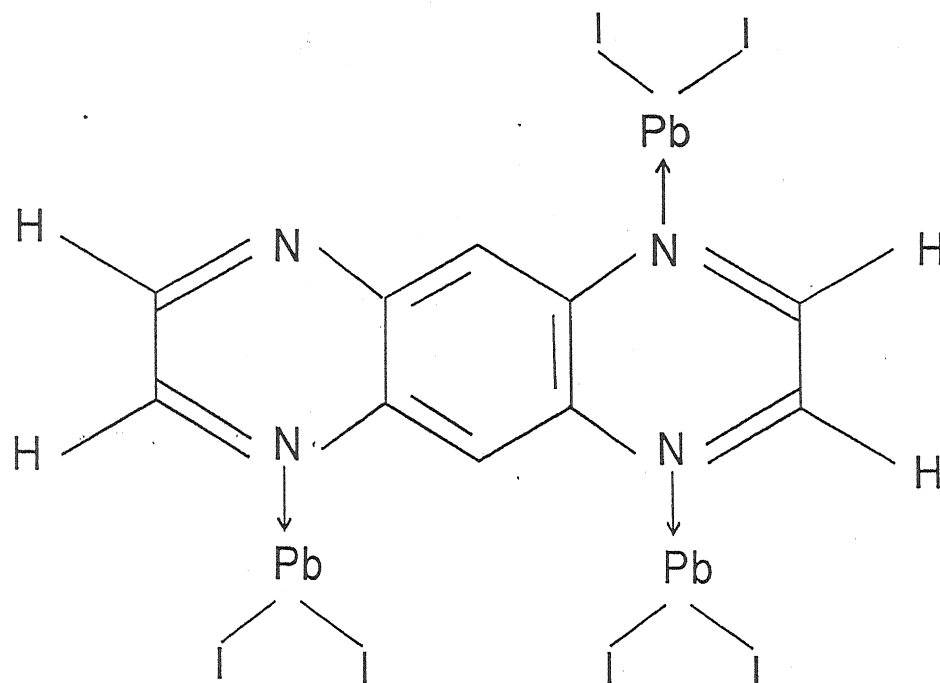
Fig. 18

Fig. 19

Fig. 20

Fig. 21

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Fig. 22

Fig. 23

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Fig. 24

Fig. 25

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Fig. 26

Fig. 27

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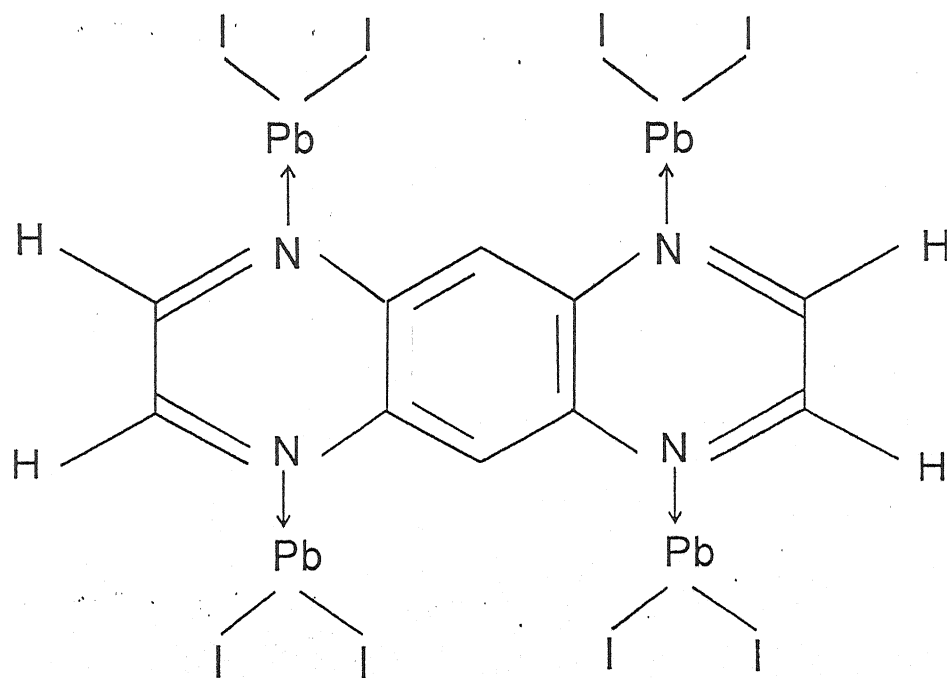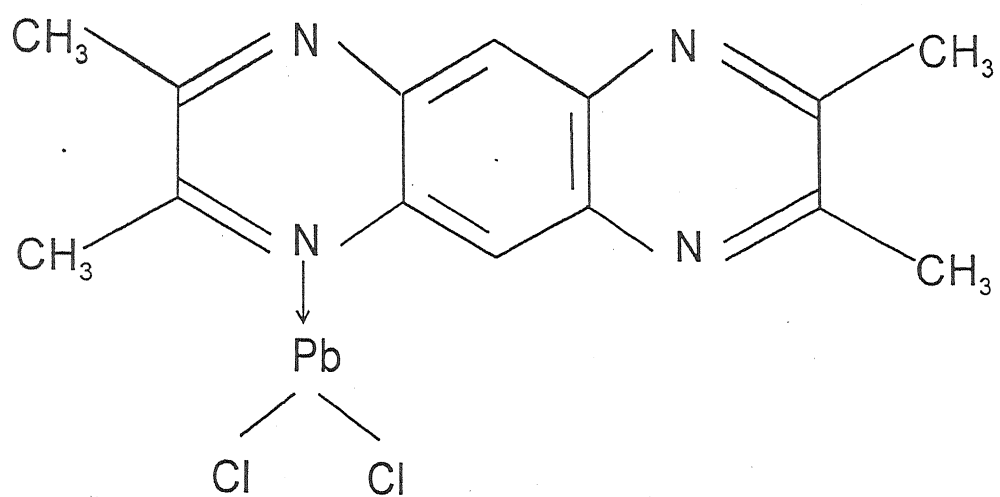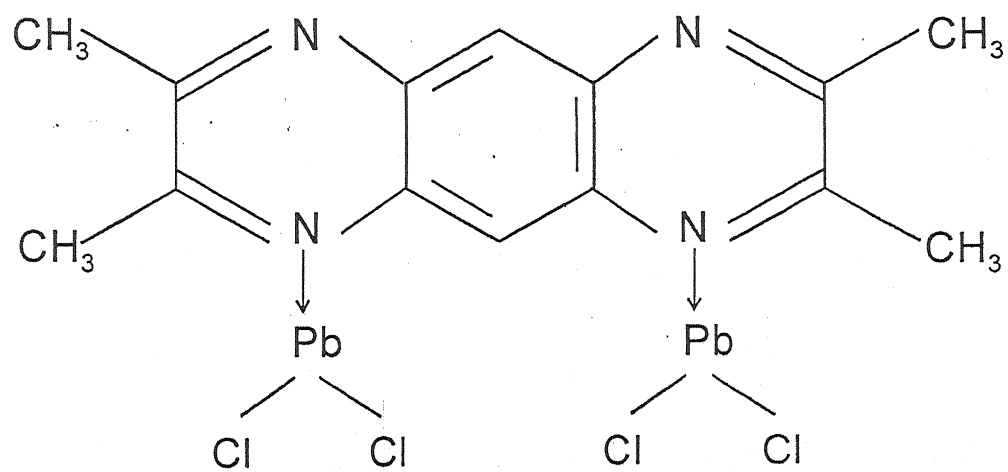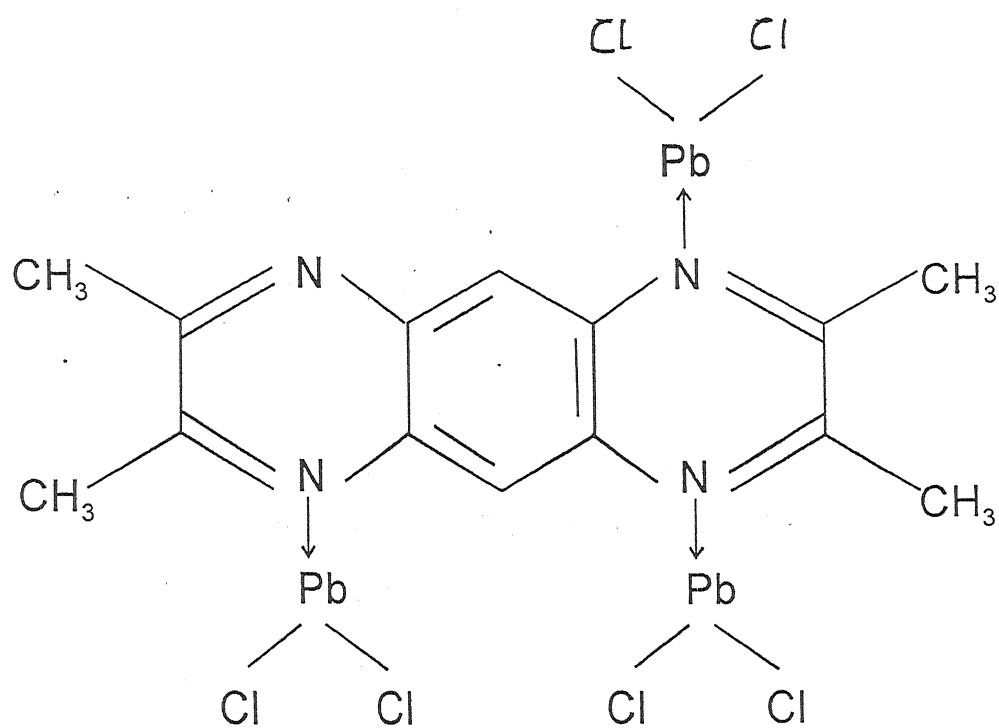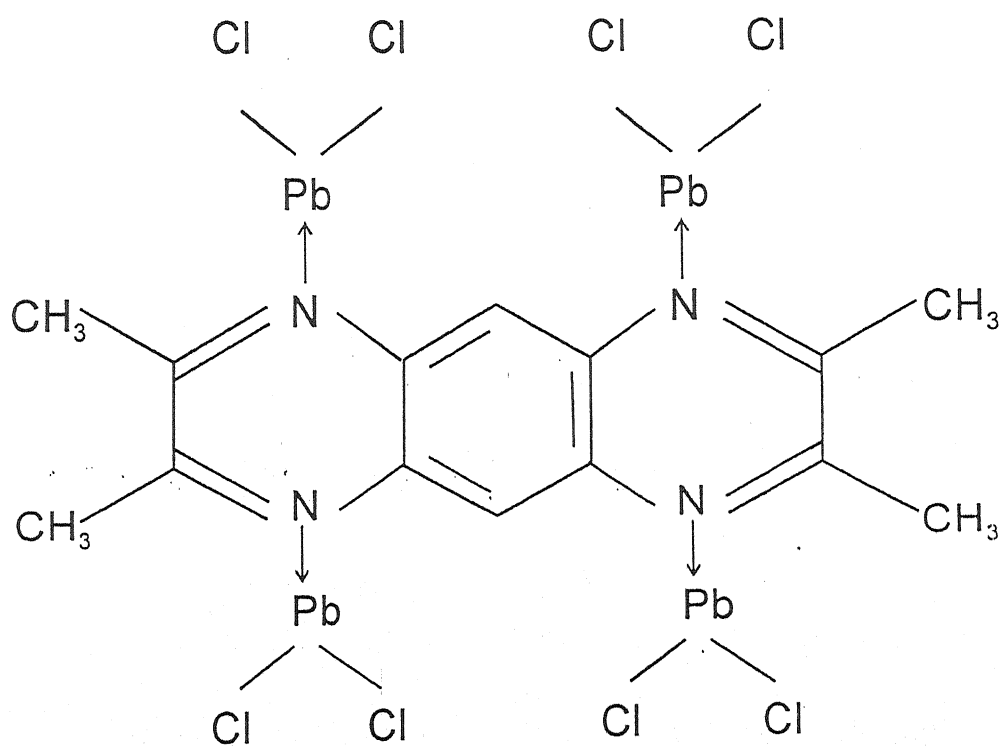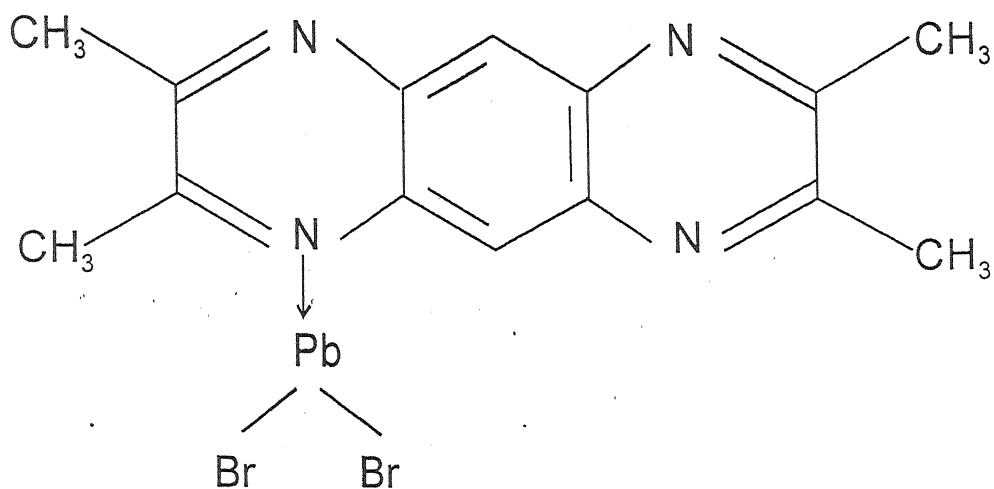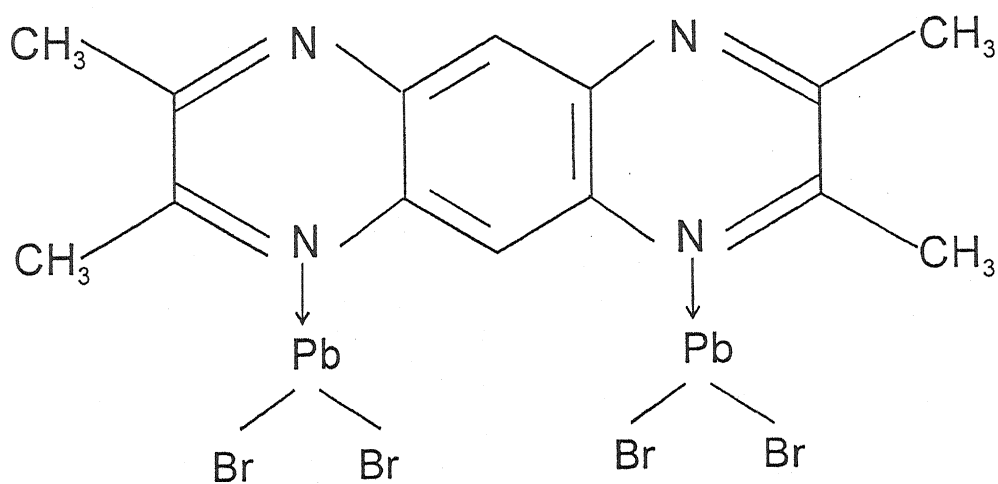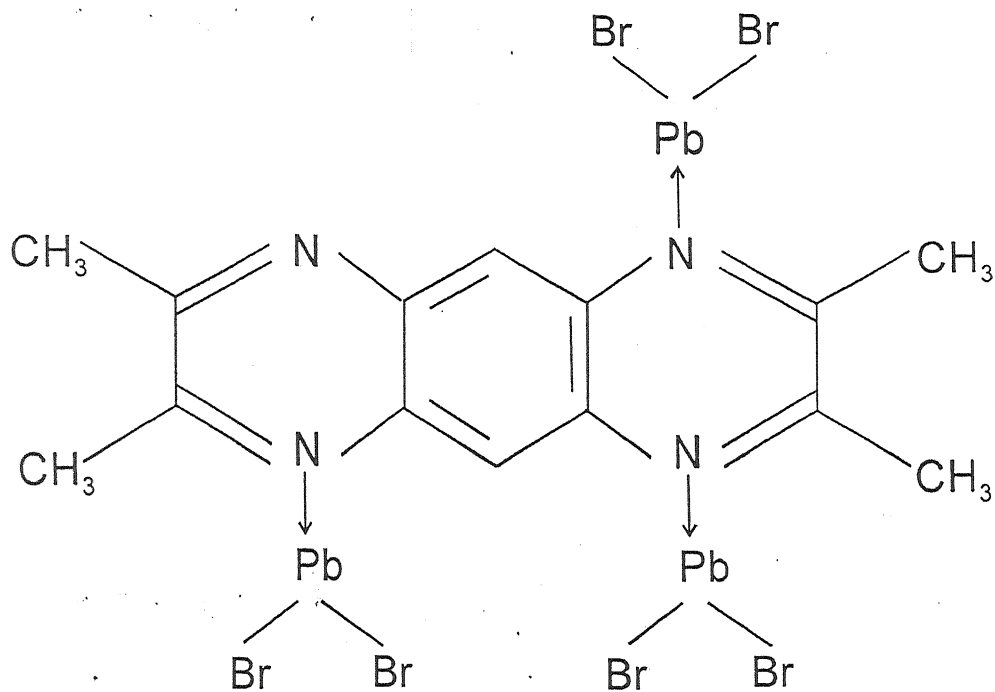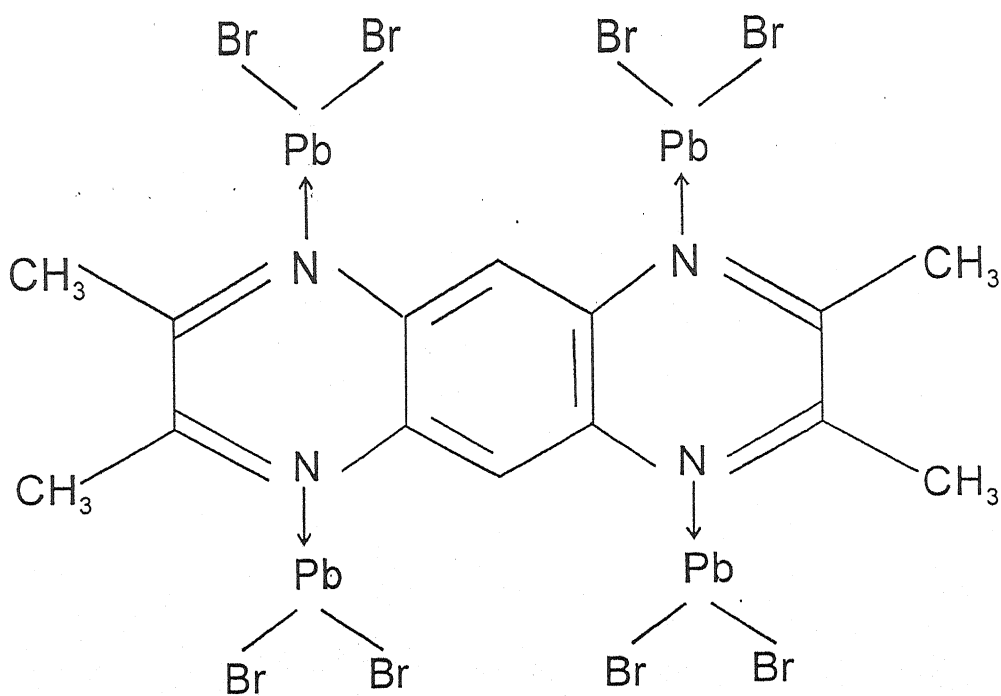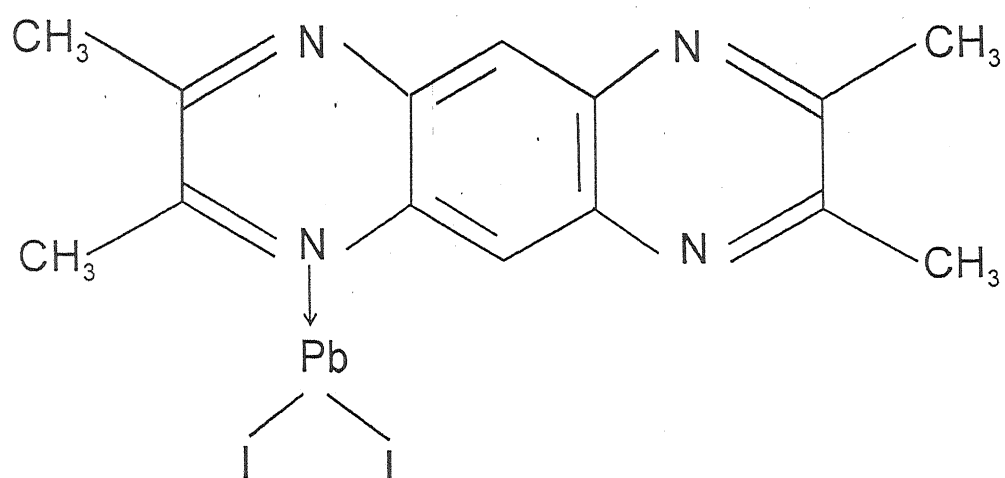
Fig. 28

Fig. 29

Fig. 30

Fig. 31

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Fig. 32

Fig. 33

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Fig. 34

Fig. 35

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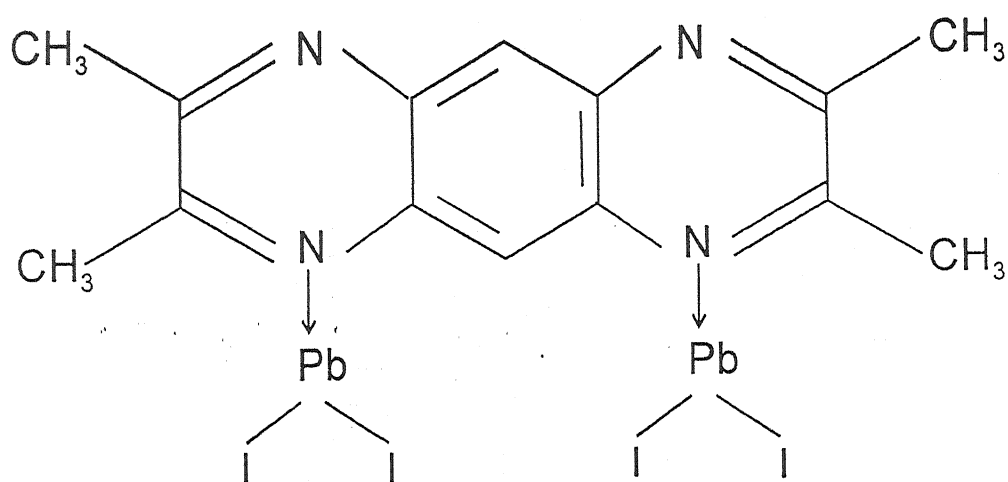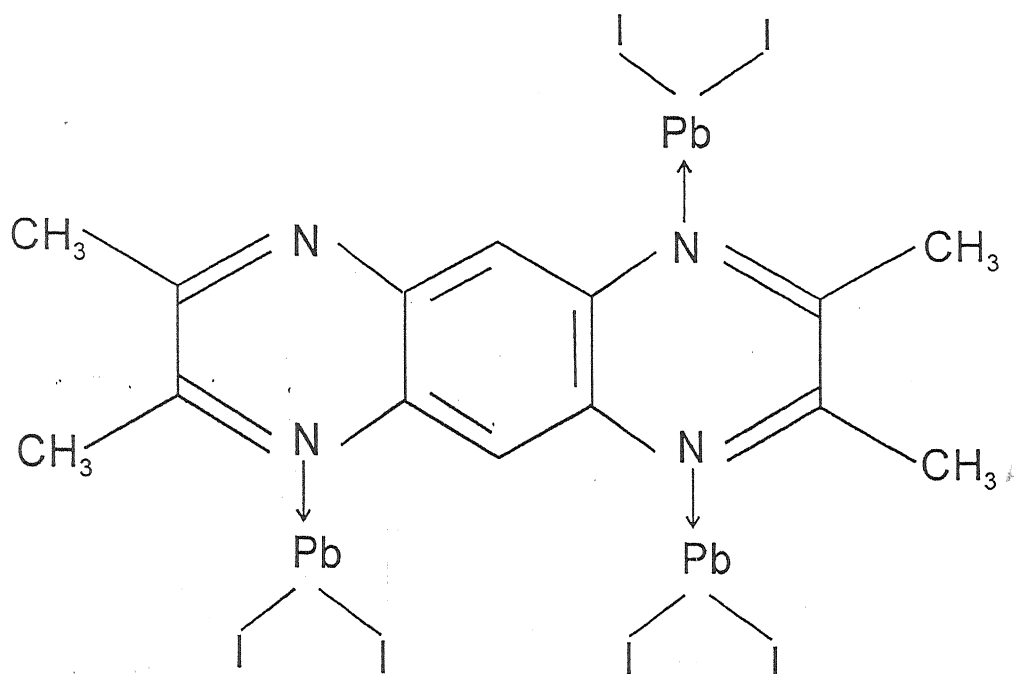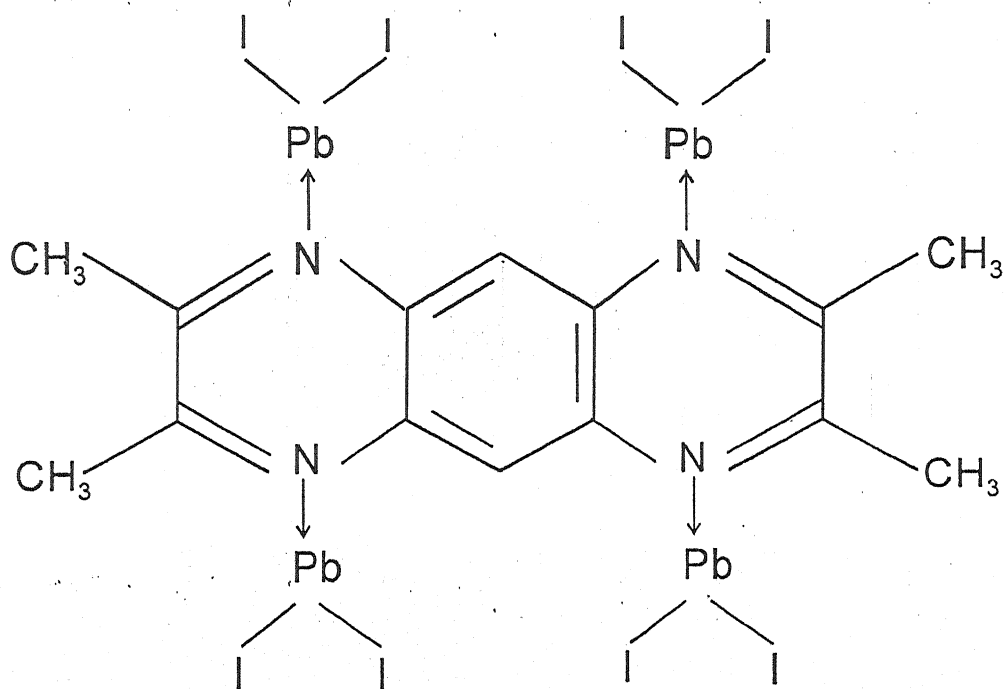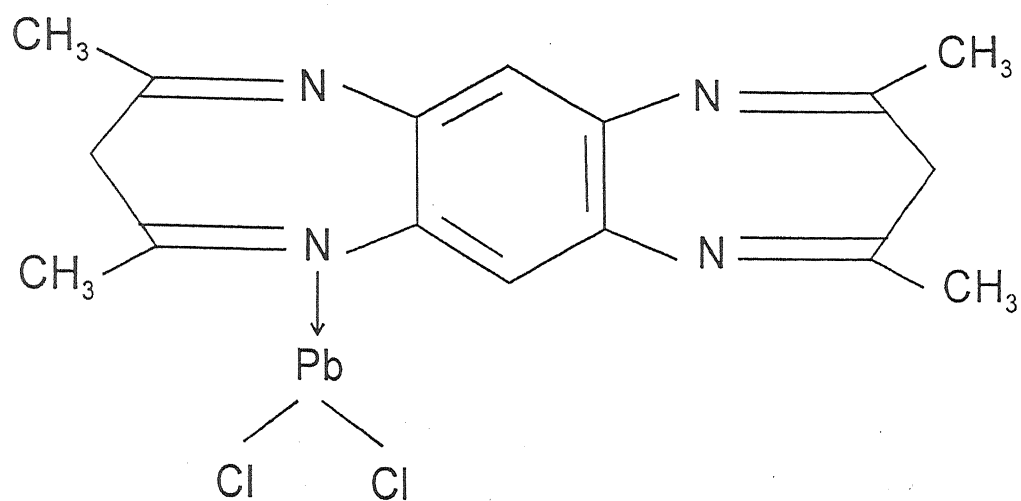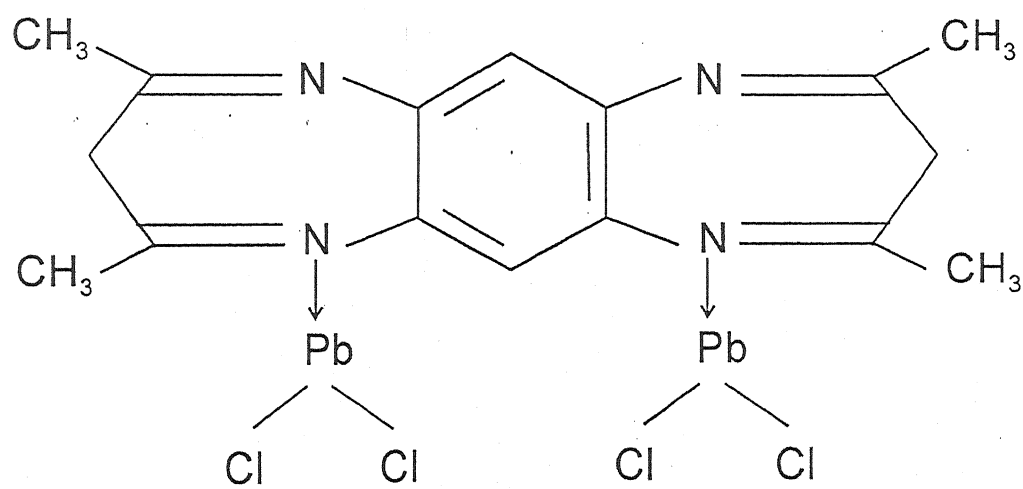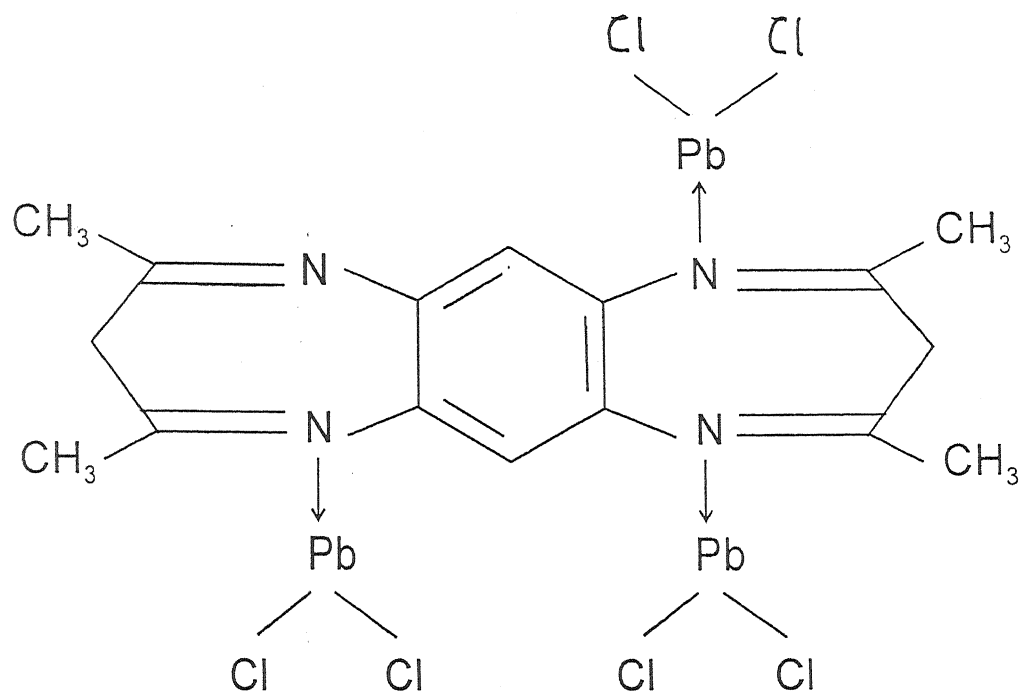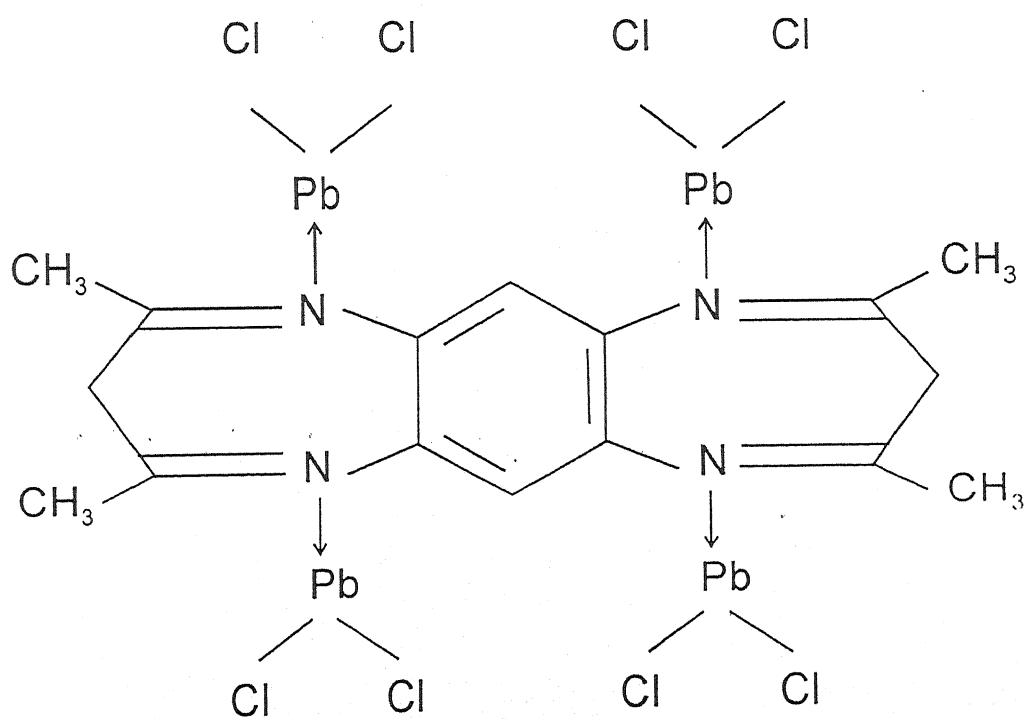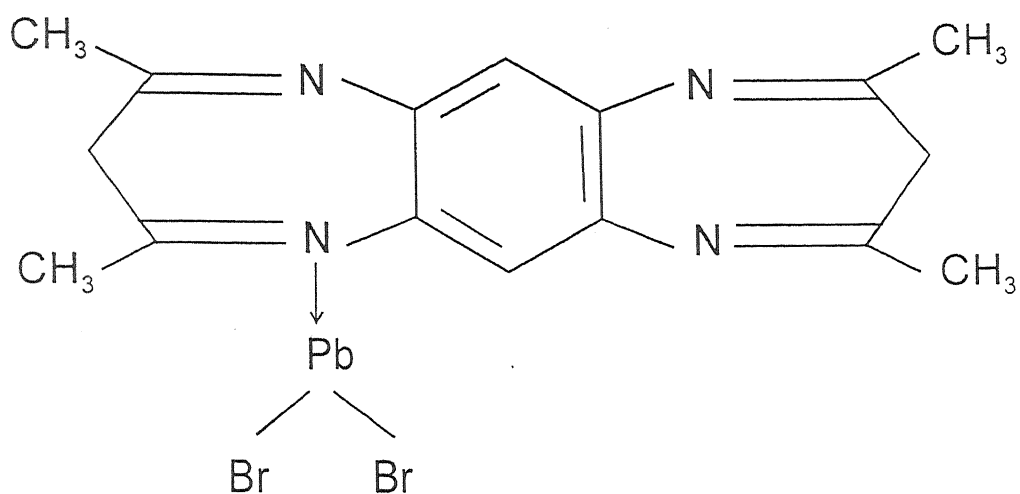
Fig. 36

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Fig. 38

Fig. 39

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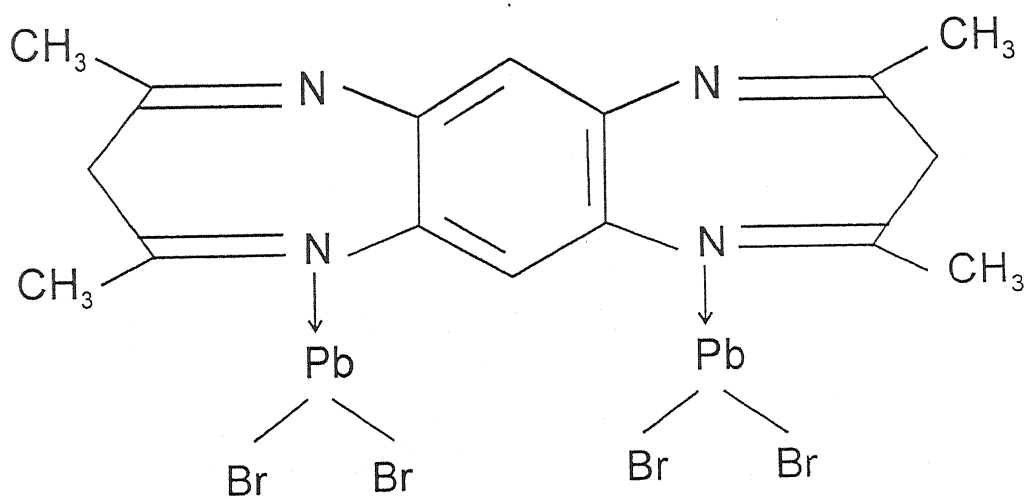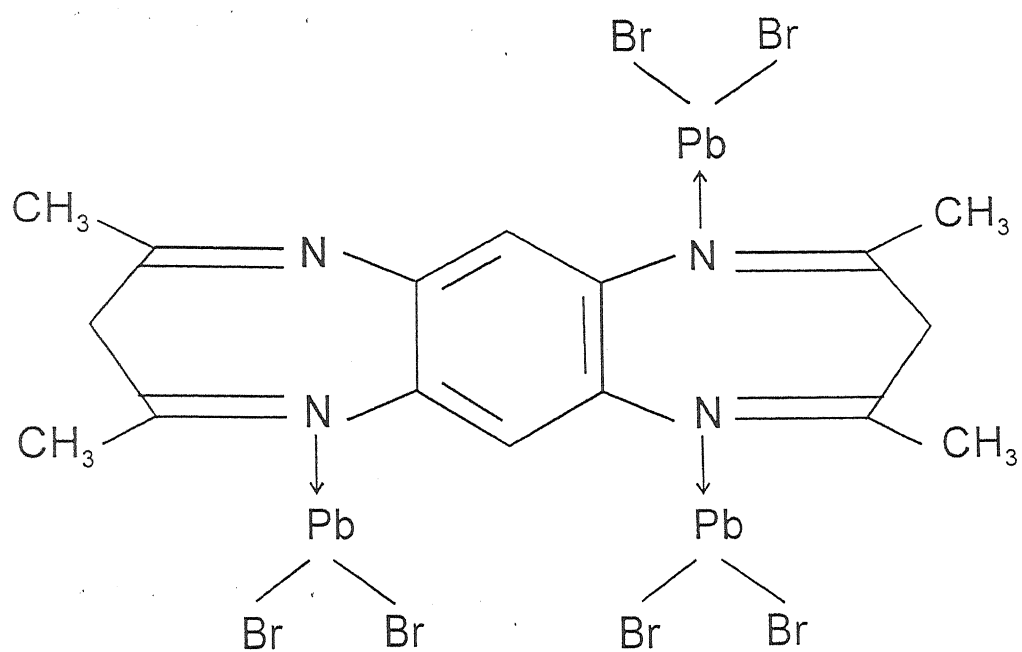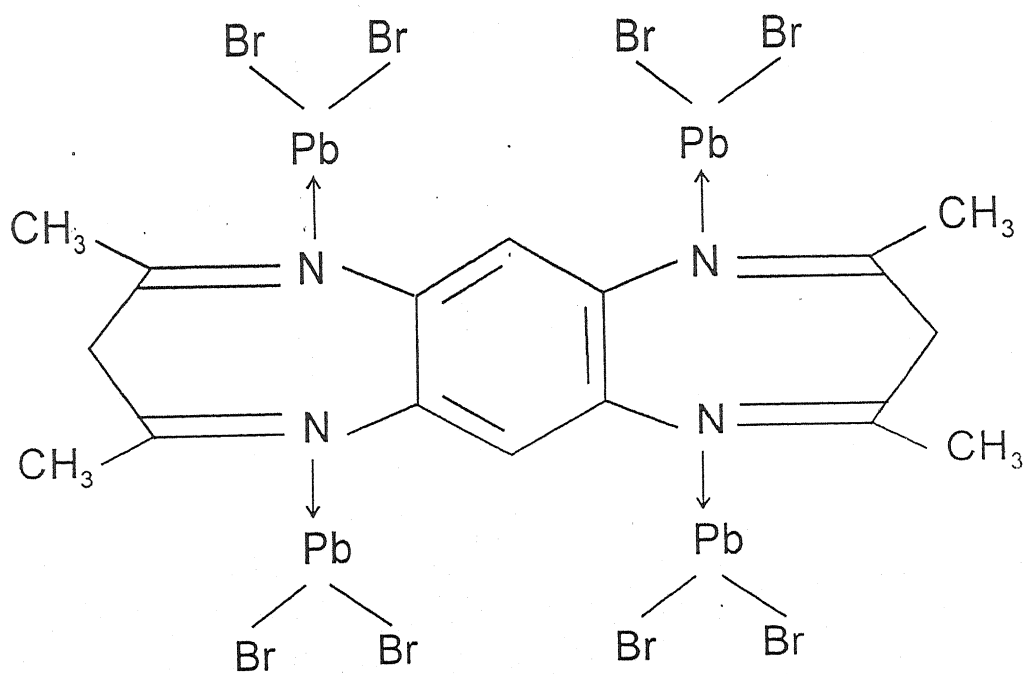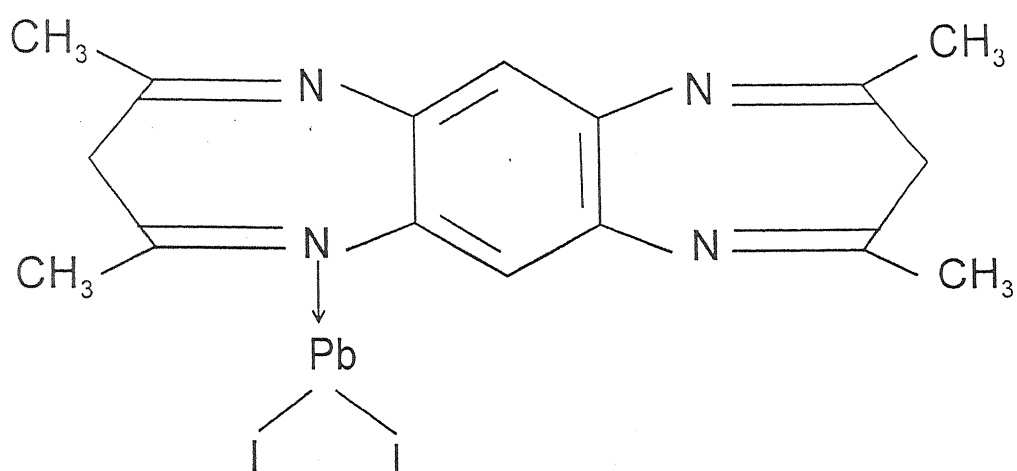
Fig. 40

Fig. 41

Fig. 42

Fig. 43

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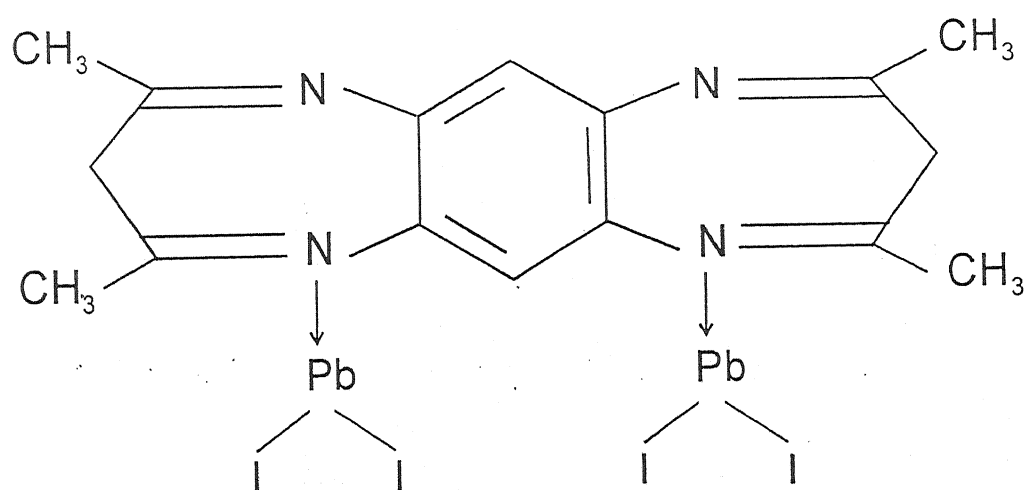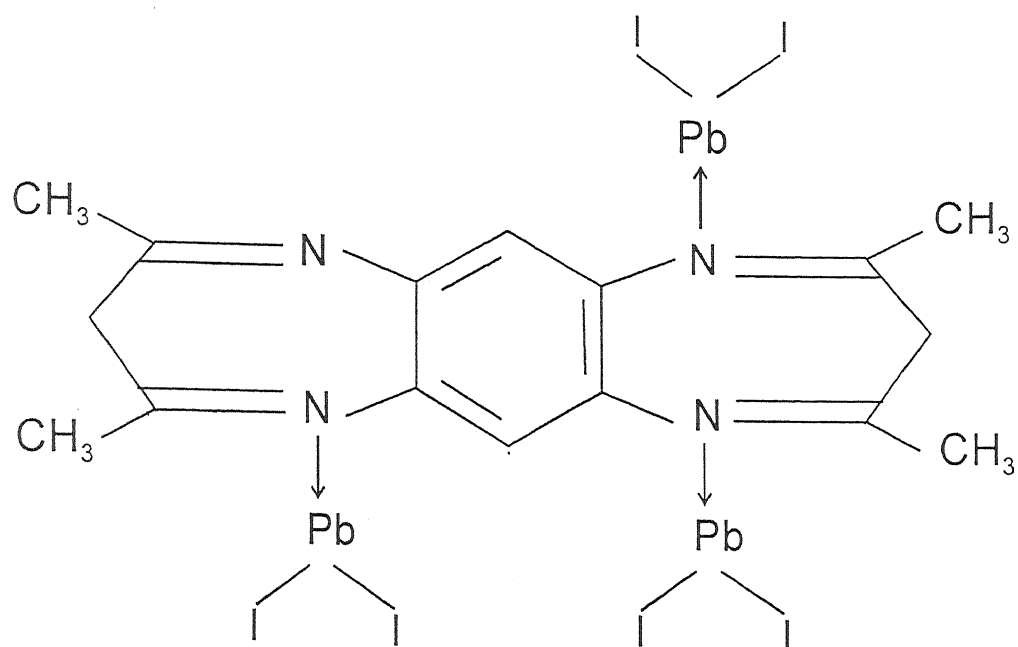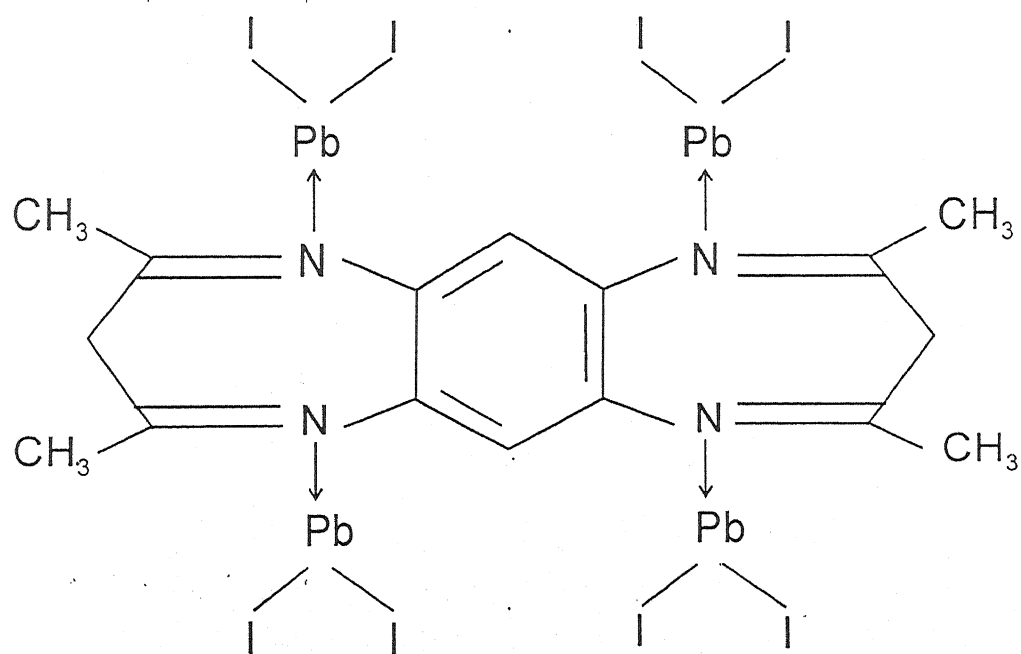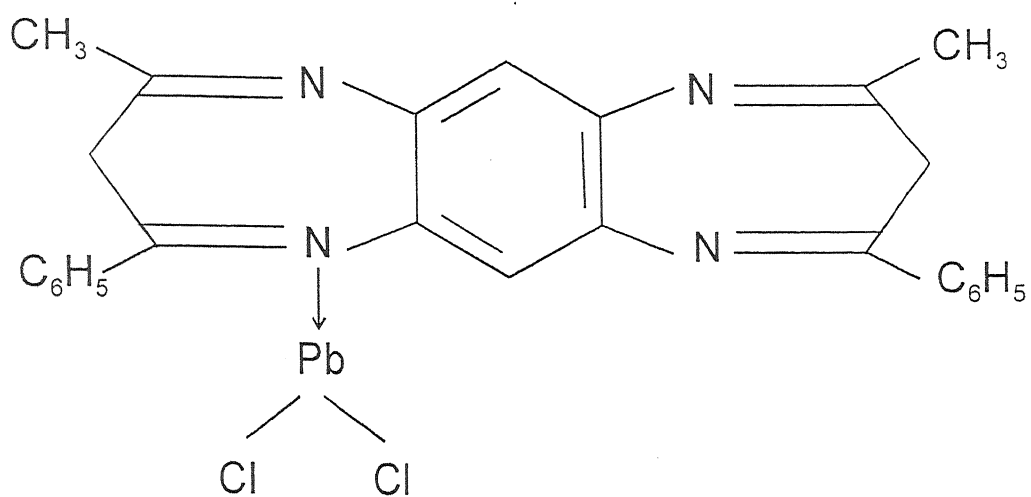
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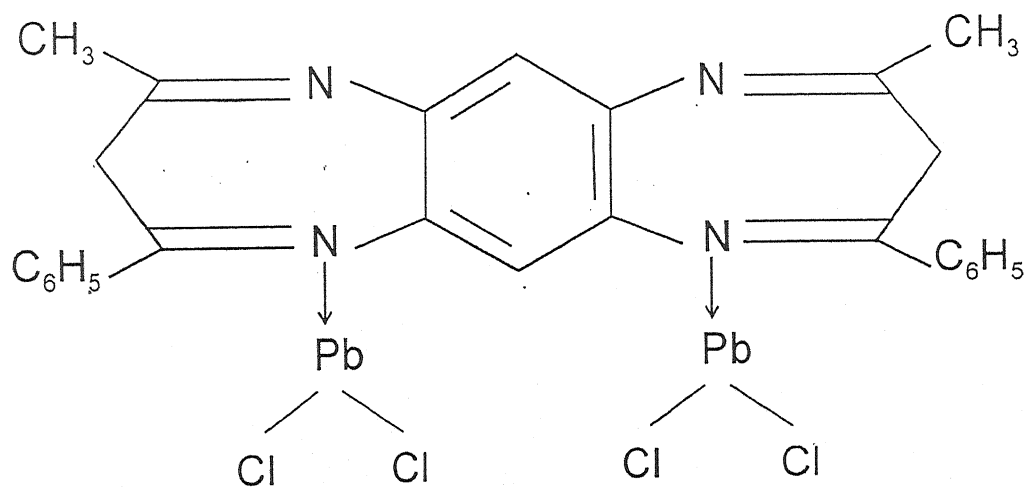
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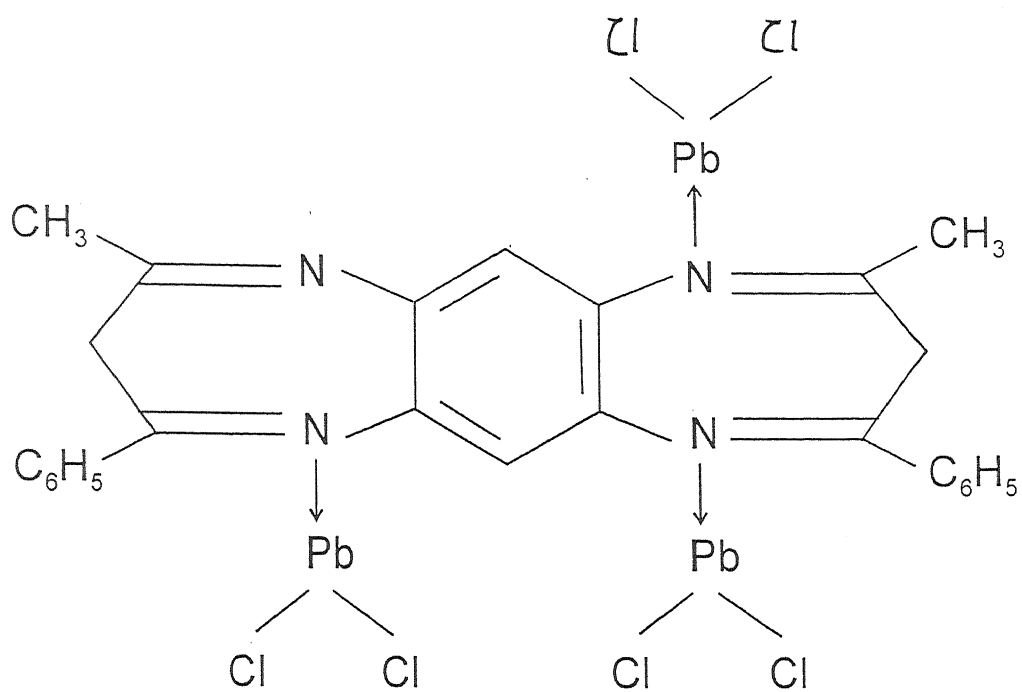
Fig. 46

Fig. 47

Fig. 48

Fig. 49

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Fig. 50

Fig. 51

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Fig. 52

Fig. 53

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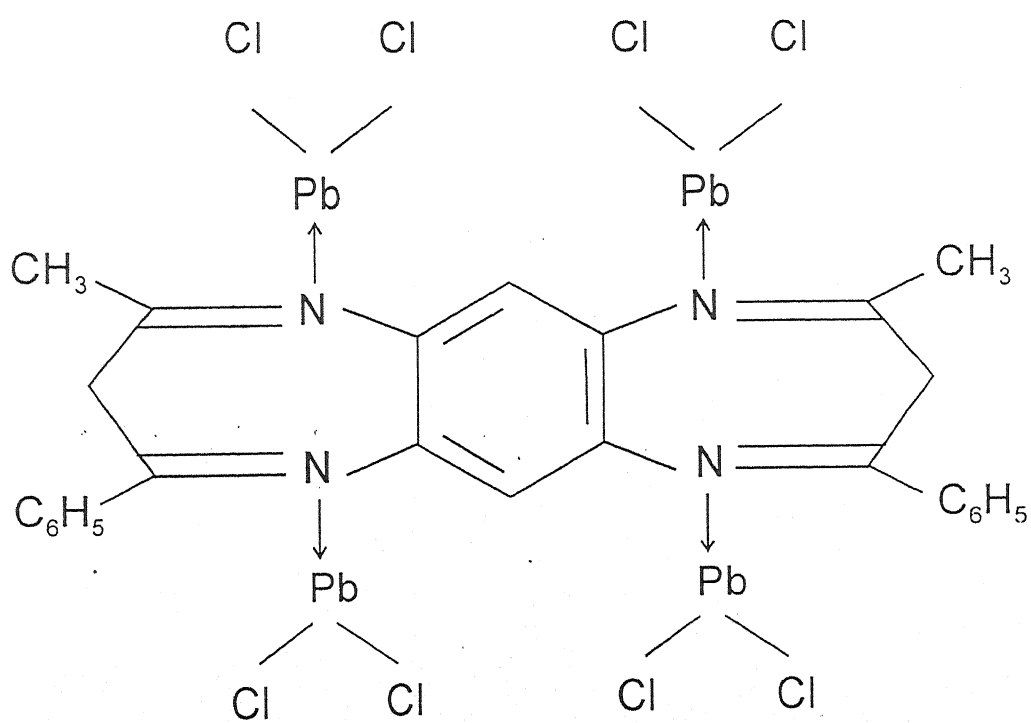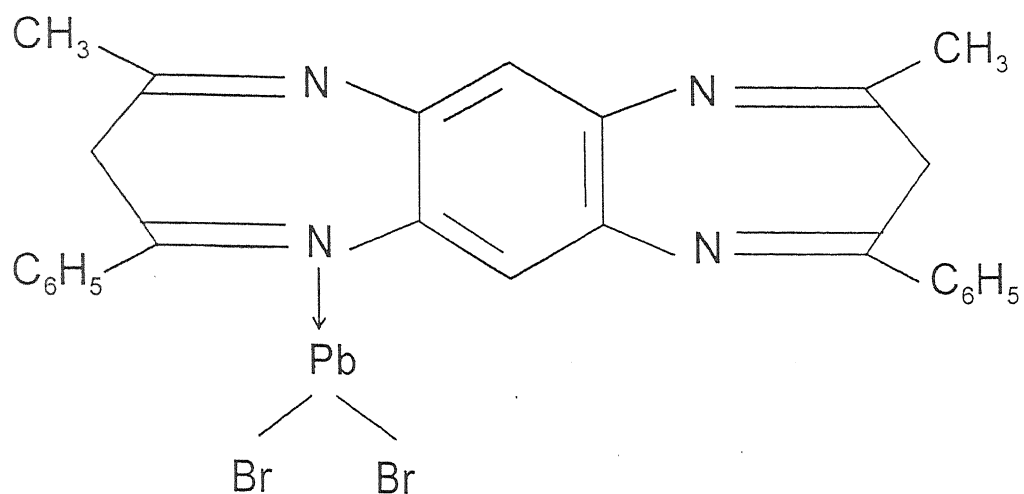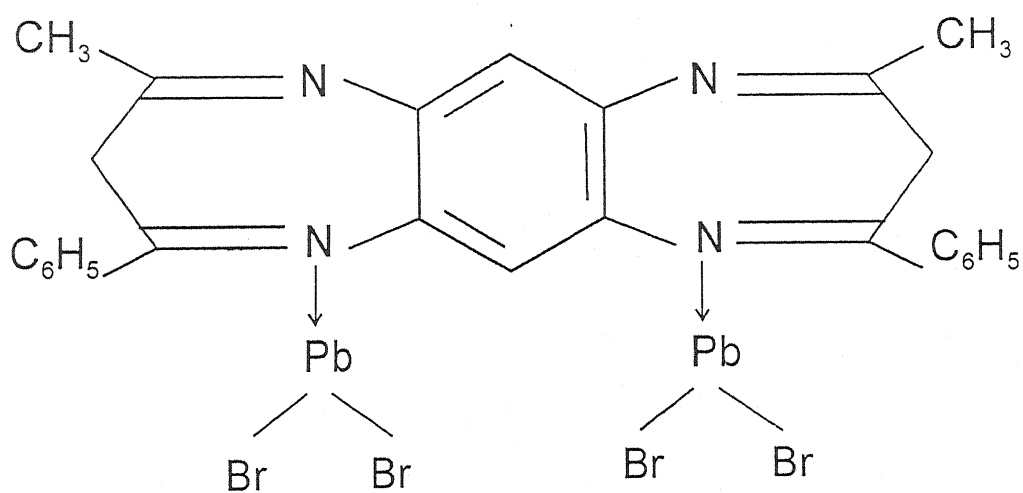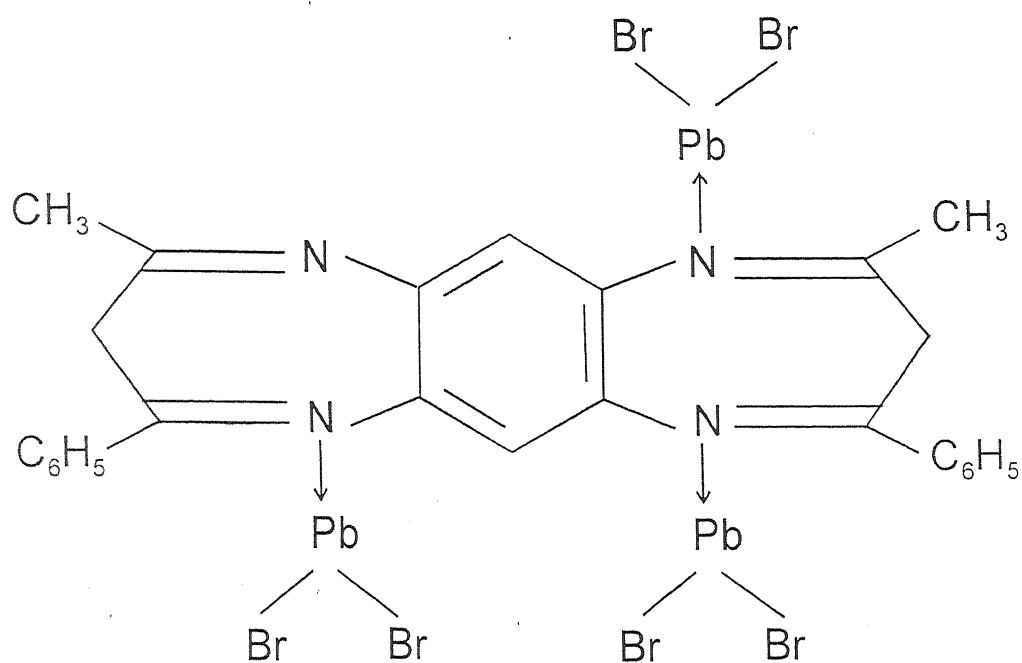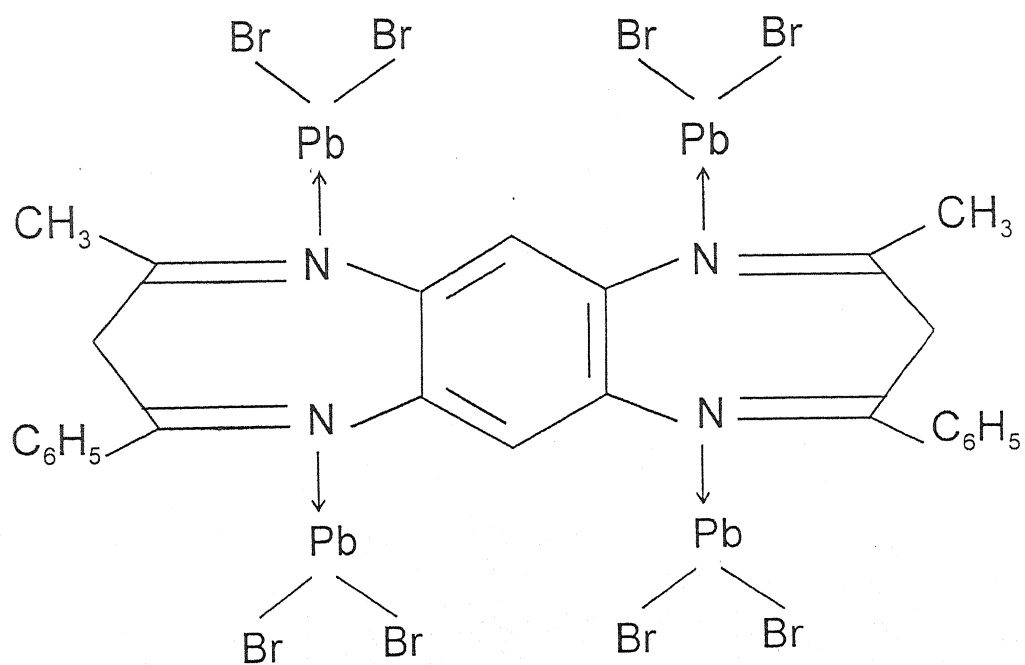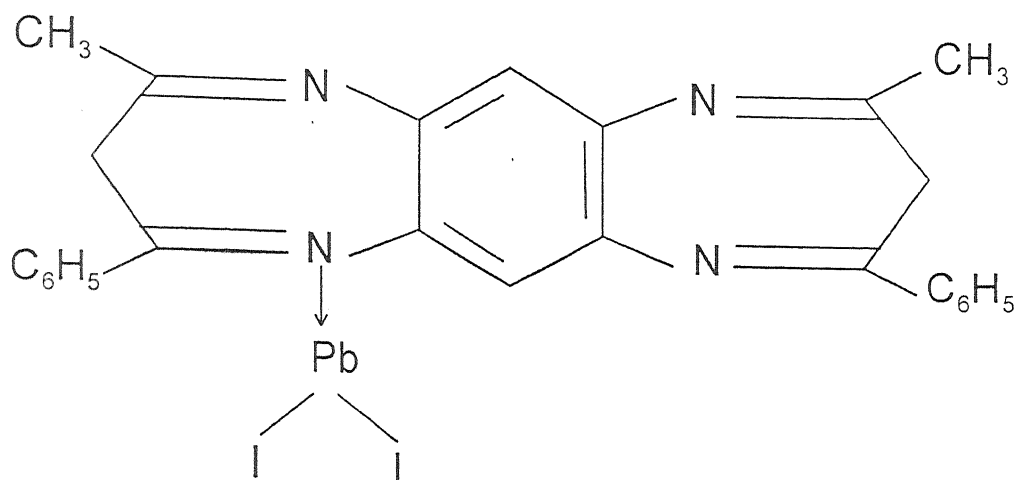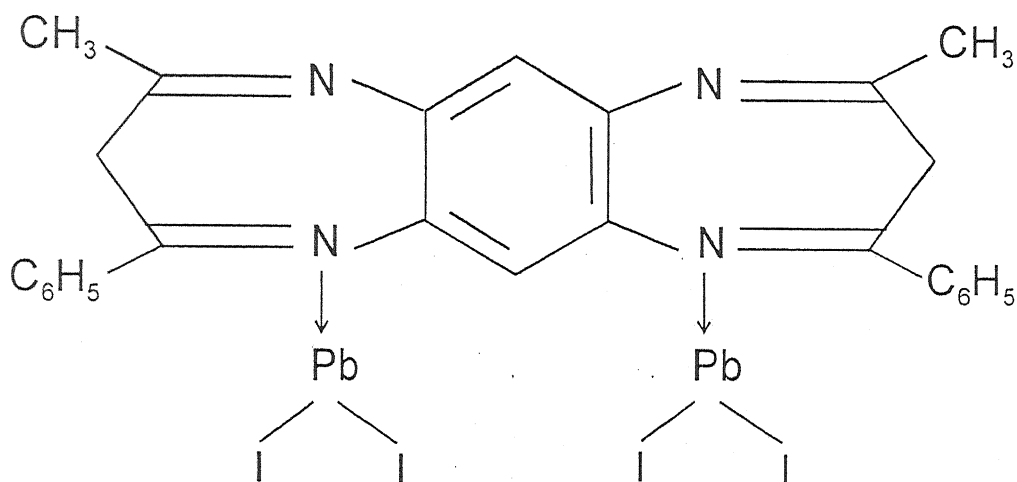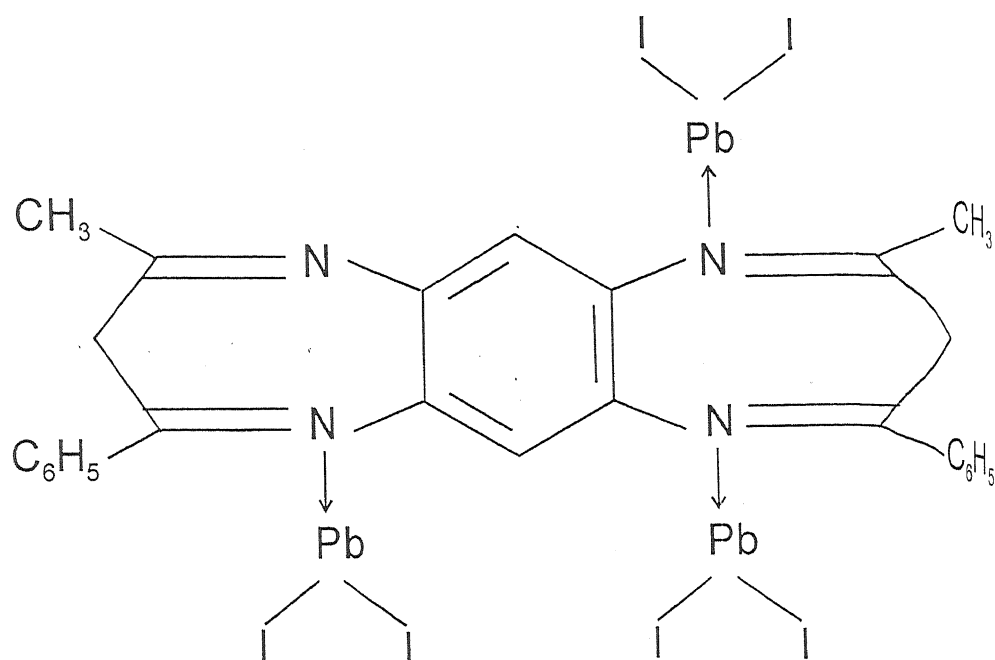
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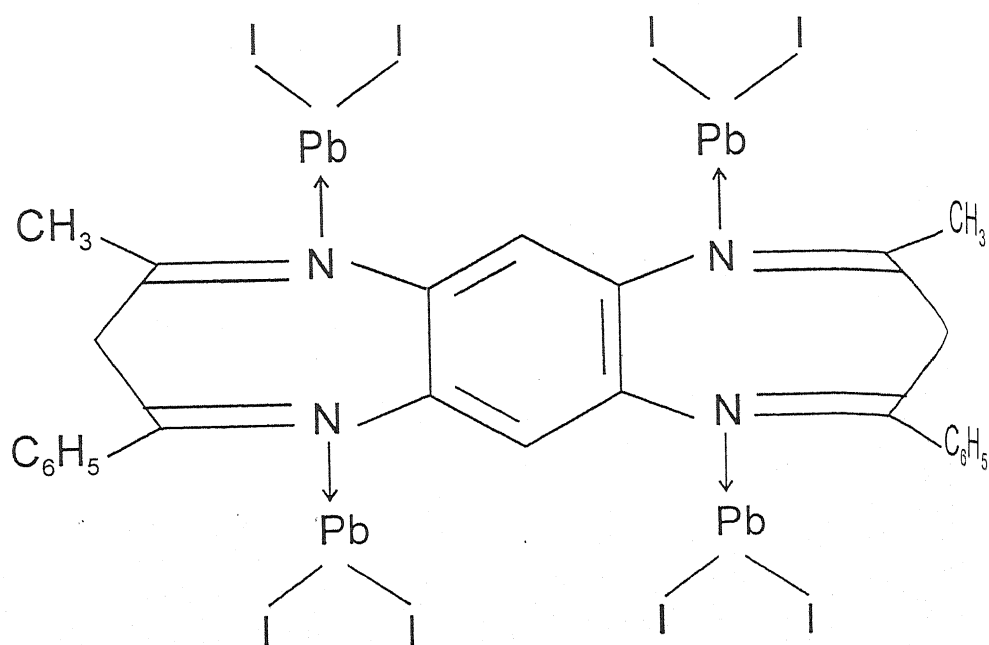
Fig. 55

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CHAPTER - IV

COMPLEXES OF PbX$_2$ WITH BIDENTATE SCHIFF BASE LIGANDS

A literature survey reveals that many Pb (II) compounds have been reported but Pb (II) compounds with Schiff base and macrocyclic Schiff base ligands are less known. [1-2]

With the ground state configuration for Pb of $6S^2 6p^2$, it forms covalent Pb (II) compounds with use of unpaired p-electrons, e.g. $PbCl_2$. The vacant one 6p orbital can be filled by donor and form compound like $[PbCl_2.D]$ with Sp^3 hybridisation. Moreover, in $[PbCl_2.D]$ Pb (II) have $6s^2$ lone pair, which can also from M $\longleftarrow$ Pb bond by donating Pb (II) $6s^2$ lone pair electron.
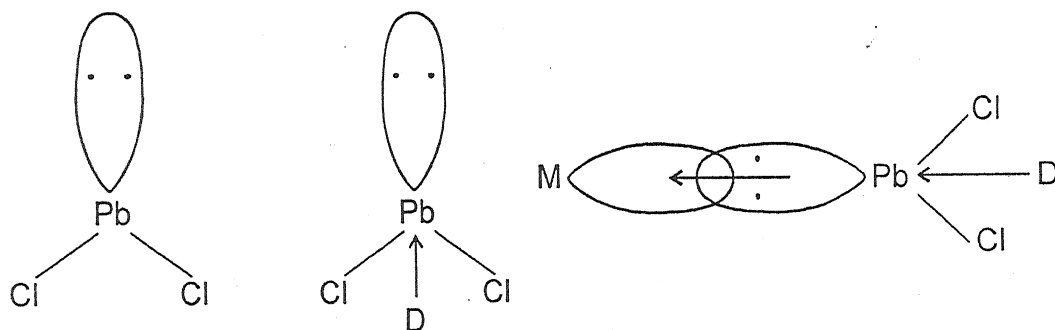
Thus Pb (II) can act both ways as acceptor and donor.

This chapter deals with interaction of Pb(II) halides i.e. $PbCl_2$, $PbBr_2$ and PbI_2 with various bidentate new Schiff base ligands. The product which will be obtained, will be characterised by various physicochemical methods to establish their structure and geometry.

EXPERIMENTAL

$PbCl_2$, $PbBr_2$ and PbI_2 are used from Aldrich.

Preparation of Schiff base ligands :

In 2mmol of 2-acetylpyrrole or 2-pyrrolecarboxy-aldehyde or 2-pyridylacarboxyaldehyde or 2-naphthylaldehyde in 50ml methanol was mixed 1mmol of cyclohexanediamine and refluxed for 3-4 hrs. The solid product was obtained, filter, washed with methanol and air-dried. The TLC has suggested the complete conversion of aldehyde to Schif base.

Thus, the following four Schiff bases are prepared:

(1)

(2-acetylpyrrole)   cyclohexane diamine   bis (2-acetylpyrrole) cyclohexanediamine

L^1

(2)

2-pyrrole-carboxyaldehyde   bis (2- pyrrolecarboxyaldehyde) cyclohexanediamine

L^2

(3)

2-pyridyl-
carboxyaldehyde

bis (2- pyridylcarboxyaldehyde)
cyclohexanediamine

L³

(4)

2naphthyl-
aldehyde

bis (2- naphthylaldehyde)
cyclohexanediamine

L⁴
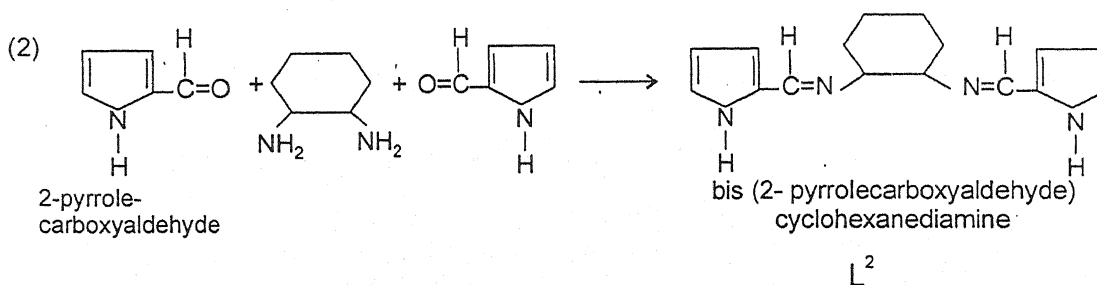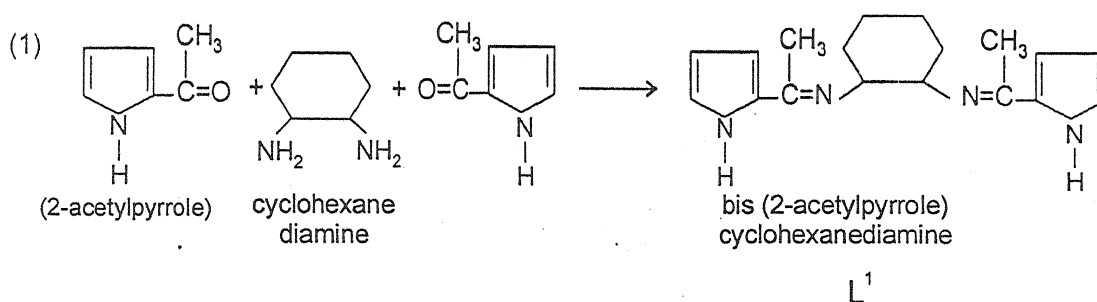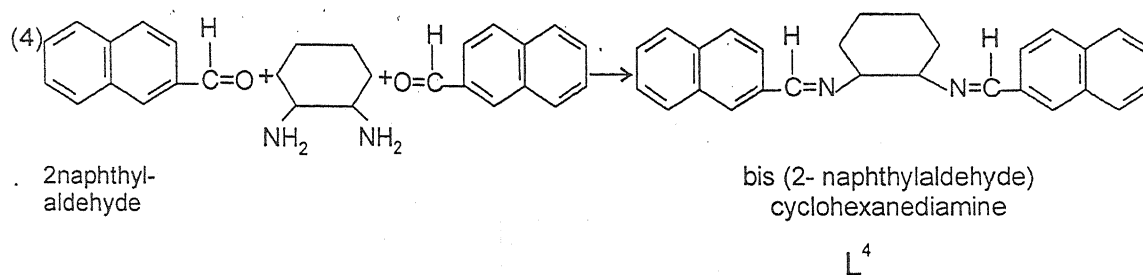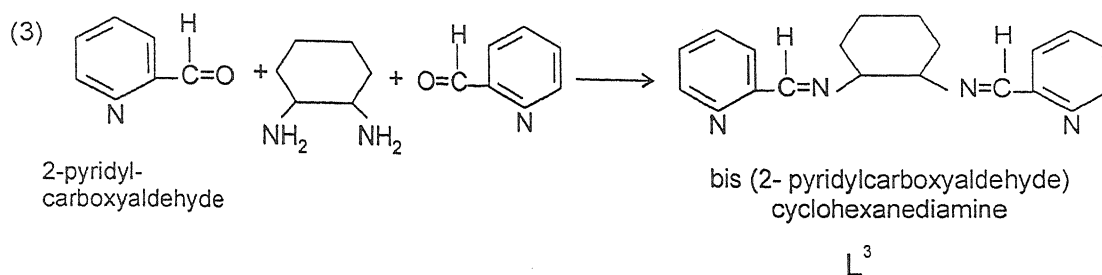
Preparation of [PbCl₂.D] complexes :

In 1mmol of PbX₂ (X= Cl or Br or I) in 50 ml CHCl₃ was mixed 1mmol of dry any above prepared Schiff base ligand and refluxed for 3-4 hrs. The solid product was obtained, filtered, washed with CHCl₃ and air-dried.

RESULTS AND DISCUSSION

The new molecular adducts have been synthesised by the interaction of PbX₂ with any prepared above Schiff base ligands:

$$PbX_2 + L \longrightarrow [PbX_2.L]$$
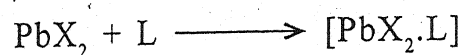
(X = Cl or Br or I)

These newly synthesised complexes are light yellow in colour. They all are stable at room temperature. The elemental analysis and molar conductance of all these prepared compunds are listed in table- I. Molar conductance of 10^{-3} M solution of the complexes were determined at room temperature. The values range from 20-30 ohm^{-1} cm^2 mol^{-1} in DMF suggested nonionic nature of all these molecular adducts.[-3].

In case of these molecular adducts, the $\gamma_{C=N}$ modes undergo shift to higher wave numbers i.e. from ligand $\gamma_{C=N}$ 1610 - 1620 cm^{-1} to molecular adduct $\gamma_{C=N}$ 1635-1670 cm^{-1}, suggesting the coordination from nitrogen atom of the ligands[4-5], Infrared frequency associated with fundamental modes of vibration of γ_{Pb-N} and γ_{Pb-Cl} was observed in the range of 305-330 cm^{-1} and 280-285 cm^{-1} [6].

The binding energies (eV) of PbX$_2$ and their prepared molecular adducts [PbX$_2$.L] for Pb2p and N1s photoelectron peaks are listed in table 2. It was observed that the binding energies of Pb2p in starting material PbX$_2$ was higher than in the prepared molecular adducts [PbX$_2$.L]. These observation suggest that the electron density on Pb(II) metal ion has increased due to coordination of ligands with Pb(II) metal ion.[7] (table [2-4] and figs [1-3]). Moreover, the value of N1s binding energy for N1s in [PbX$_2$.L]

molecular adducts have been noticed increased than free ligands (table 5 and fig 4). This also concluded coordination of nitrogen atom with metal ion of Pbx_2 [7].

On the basis of elemental analysis, moler conductivity data showing that all these molecular adducts are nonionic and IR and X-ray photoelectron spectra (XPS) results showing the site of coordination, it is possible to assign a structure for each adduct as shown in figs 5-16.

All these molecular adducts are having trigonal bipyramidal geometry i.e. sp^3d hybridisation as shown below:
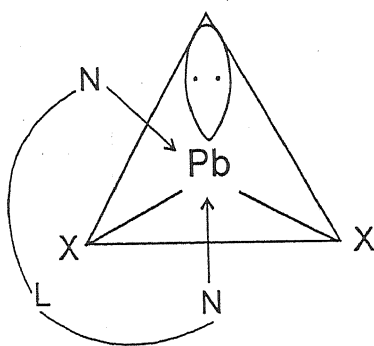
structure of $[PbX_2.L]$

Table- 1 : Aanlytical data of $[PbX_2.L]$ compounds.

S.No.	Compound	% found (calculated)			Molar conductance in DMF ohm^{-1} cm^2 mol^{-1}
		C	H	N	
1.	$[PbCl_2.L^1]$	37.6 (37.7)	3.6 (3.8)	9.6 (9.7)	10
2.	$[PbBr_2.L^1]$	32.4 (32.6)	3.3 (3.3)	8.0 (8.4)	20
3.	$[PbI_2.L^1]$	25.0 (25.2)	2.4 (2.5)	6.4 (6.5)	22
4.	$[PbCl_2.L^2]$	35.0 (35.2)	3.2 (3.3)	10.0 (10.2)	26
5.	$[PbBr_2.L^2]$	30.2 (30.3)	2.6 (2.8)	8.6 (8.8)	22
6.	$[PbI_2.L^2]$	26.2 (26.4)	2.4 (2.4)	7.6 (7.6)	16
7.	$[PbCl_2.L^3]$	38.0 (38.0)	3.0 (3.1)	9.6 (9.8)	14
8.	$[PbBr_2.L^3]$	32.6 (32.8)	2.6 (2.7)	8.4 (8.5)	12
9.	$[PbI_2.L^3]$	28.6 (28.7)	2.3 (2.3)	7.2 (7.4)	10
10.	$[PbCl_2.L^4]$	50.2 (50.4)	3.6 (3.6)	4.0 (4.2)	12
11.	$[PbBr_2.L^4]$	44.2 (44.4)	3.0 (3.1)	3.6 (3.7)	16
12.	$[PbI_2.L^4]$	39.4 (39.5)	2.8 (2.8)	3.2 (3.2)	12

Table- 2 : Pb2p binding energy (eV) $PbCl_2$ and $[PbCl_2.L]$ complexes.

S.No.	Compound	Pb2p
1.	$PbCl_2$	764.8
2.	$[PbCl_2L^1]$	763.6
3.	$[PbCl_2L^2]$	763.6
4.	$[PbCl_2L^3]$	763.6
5.	$[PbCl_2L^4]$	763.6

Table- 3 : Pb2p binding energy (eV) $PbBr_2$ and $[PbBr_2.L]$ complexes.

S.No.	Compound	Pb2p
1.	$PbBr_2$	764.6
2.	$[PbBr_2L^1]$	763.4
3.	$[PbBr_2L^2]$	763.4
4.	$[PbBr_2L^3]$	763.4
5.	$[PbBr_2L^4]$	763.4

Table- 4 : Pb2p binding energy (eV) PbI_2 and $[PbI_2.L]$ complexes.

S.No.	Compound	Pb2p
1.	PbI_2	764.4
2.	$[PbI_2L^1]$	763.2
3.	$[PbI_2L^2]$	763.2
4.	$[PbI_2L^3]$	763.2
5.	$[PbI_2L^4]$	763.2

Table- 5 : N1s binding energy (eV) in ligand and [PbX$_2$.L] complexes.

S.No.	Ligand & Compound	N1s
1.	Ligand L^1	400.8
2.	[PbCl$_2$.L^1]	403.6
3.	[PbBr$_2$.L^1]	403.6
4.	[PbI$_2$.L^1]	403.6
5.	Ligand L^2	400.8
6.	[PbCl$_2$.L^2]	403.6
7.	[PbBr$_2$.L^2]	403.6
8.	[PbI$_2$.L^2]	403.6
9.	Ligand L^3	400.8
10	[PbCl$_2$.L^3]	403.4
11.	[PbBr$_2$.L^3]	403.4
12.	[PbI$_2$.L^3]	403.4
13.	Ligand L^4	400.8
14.	[PbCl$_2$.L^4]	403.4
15.	[PbBr$_2$.L^4]	403.4
16.	[PbI$_2$.L^4]	403.4

Pb2p photoelectron peak
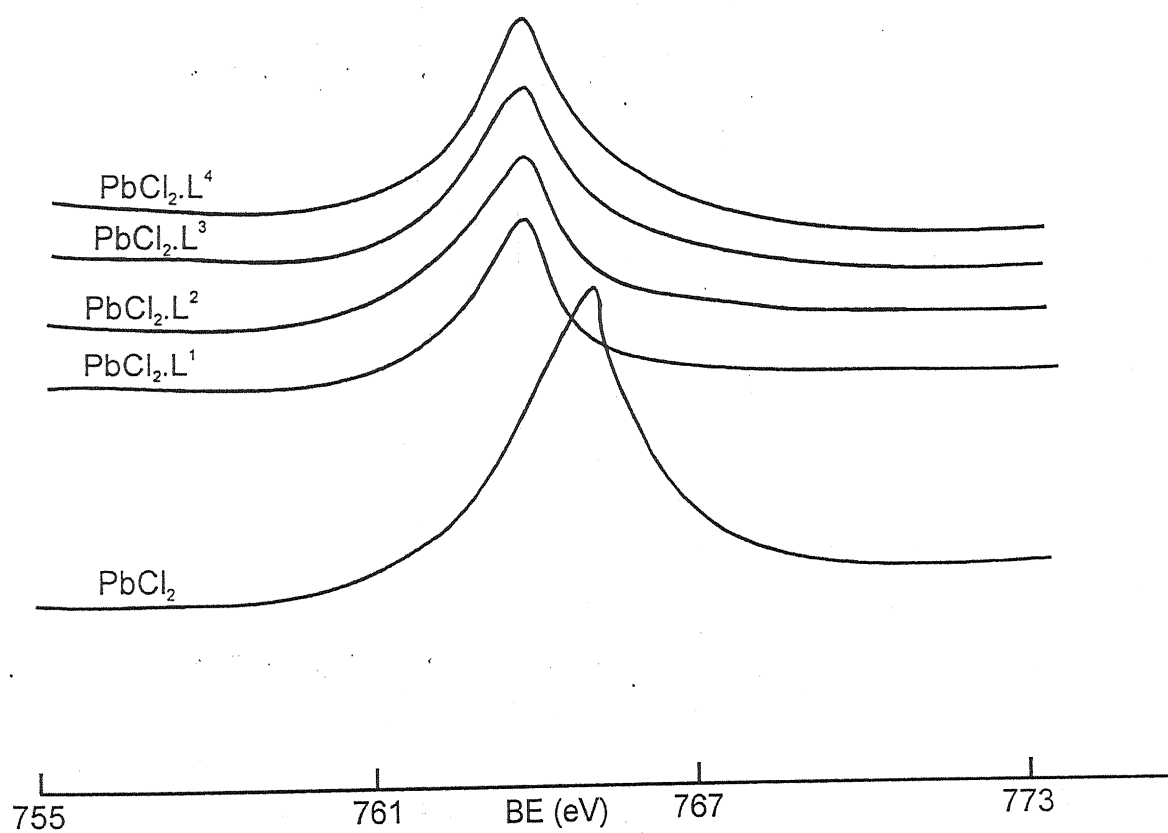
Fig.1 : Pb2p binding energies (eV) in $PbCl_2$ and $[PbCl_2.L]$ Complexes.

Pb2p photoelectron peak
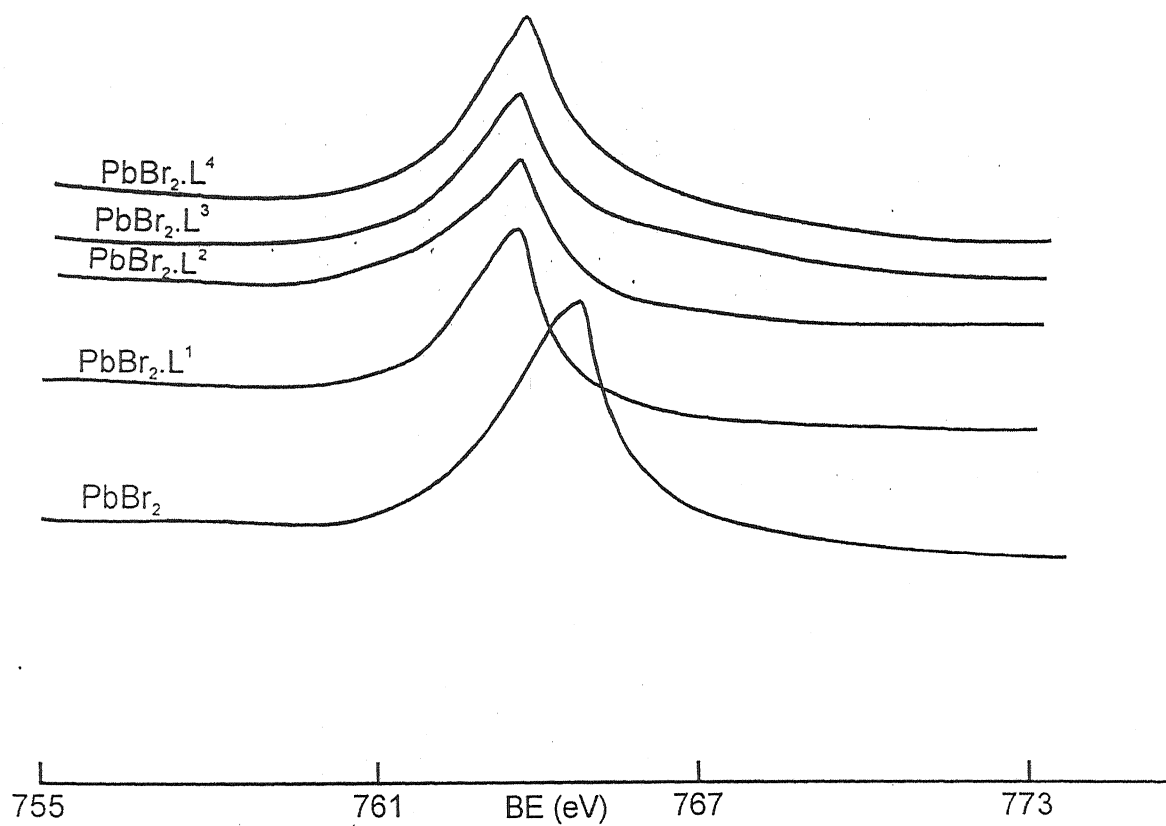
Fig.2 : Pb2p binding energies (eV) in $PbBr_2$ and $[PbBr_2.L]$ Complexes.

Pb2p photoelectron peak
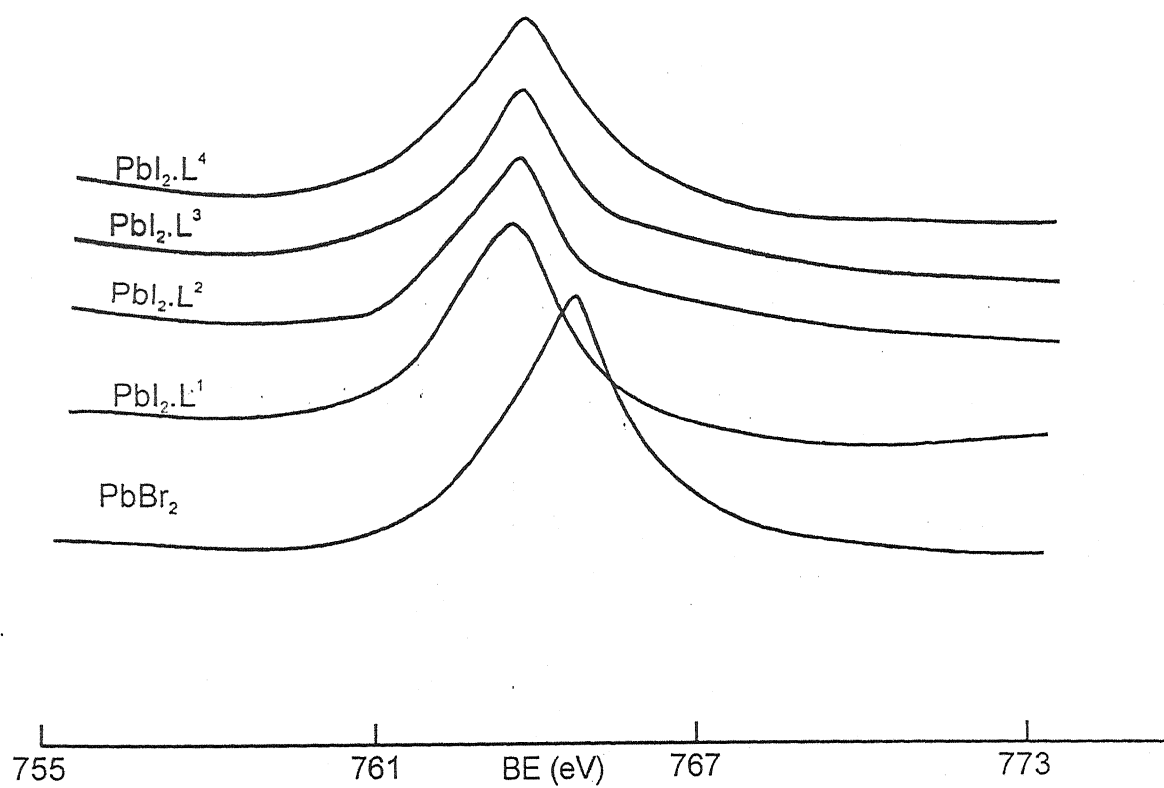
Fig.3 : Pb2p binding energies (eV) in PbI_2 and [PbI_2.L] Complexes.

N1s photoelectron peak

PbI$_2$.L^4

PbBr$_2$.L^4

PbCl$_2$.L^4

Ligand L^4

PbI$_2$.L^3

PbBr$_2$.L^3

PbCl$_2$.L^3

Ligand L^3

PbI$_2$.L^2

PbBr$_2$.L^2

PbCl$_2$.L^2

Ligand L^2

PbI$_2$.L^1

PbBr$_2$.L^1

PbCl$_2$.L^1

Ligand L^1

390   396   BE (eV)   402   408
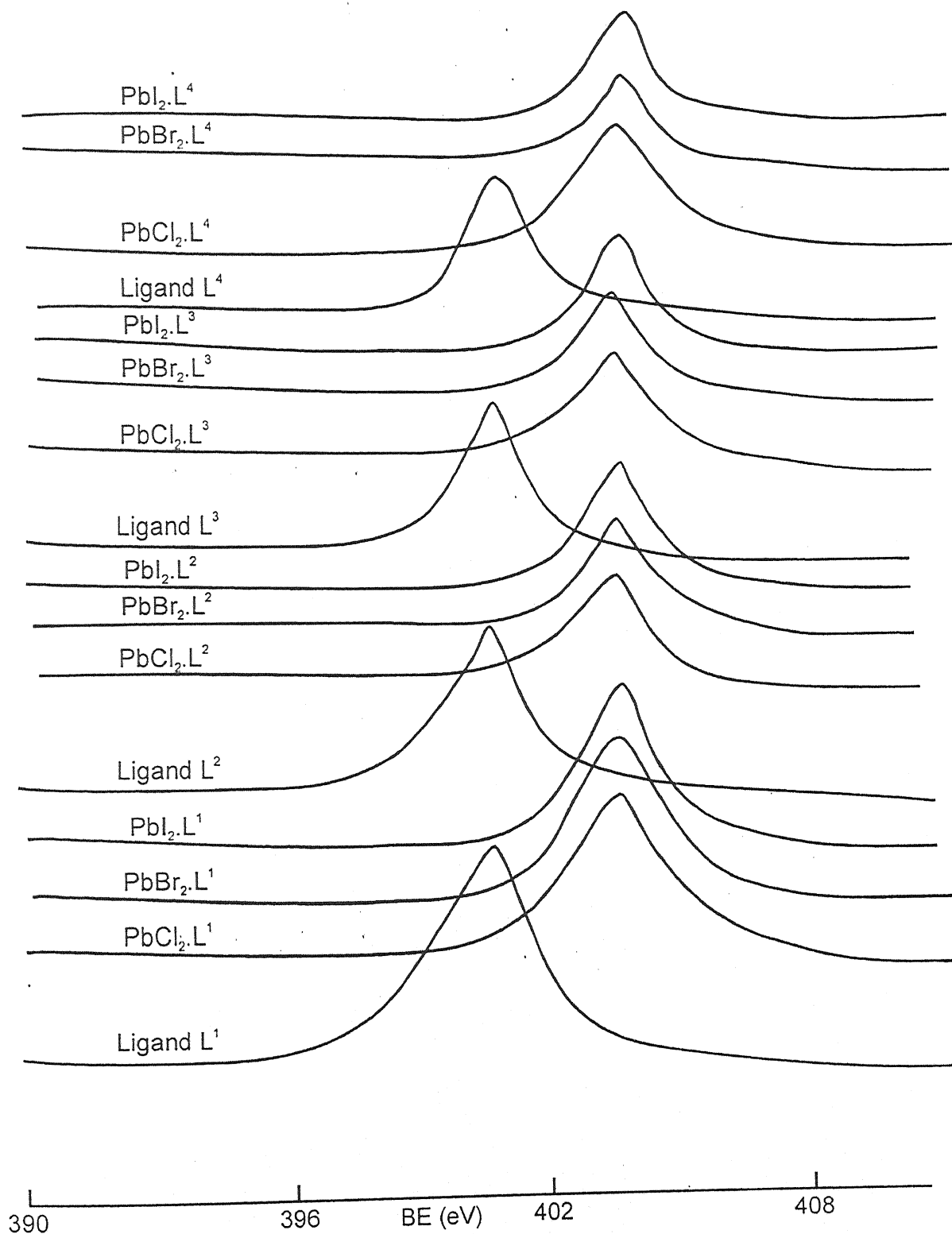
Fig.4 : N1s binding energies (eV) in ligand and [PbX$_2$.L] Complexes.

148

Fig. 5

Fig. 6

149

Fig. 7

Fig. 8

150

Fig. 9

Fig. 10

151

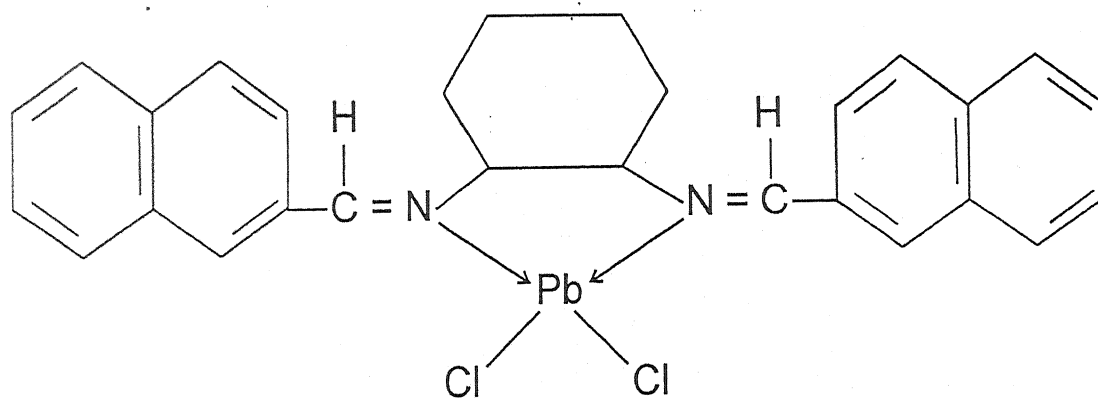**Fig. 11**

Fig. 12
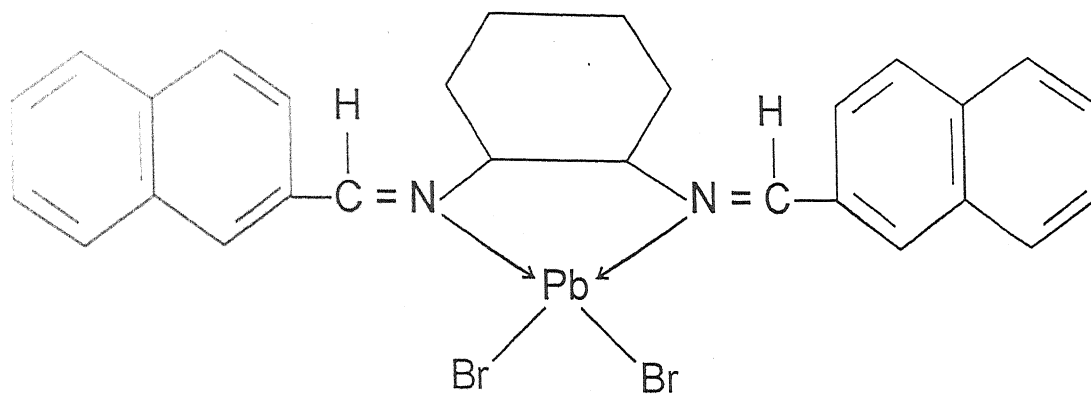
152

Fig. 13

Fig. 14

153

Fig. 15

Fig. 16

154
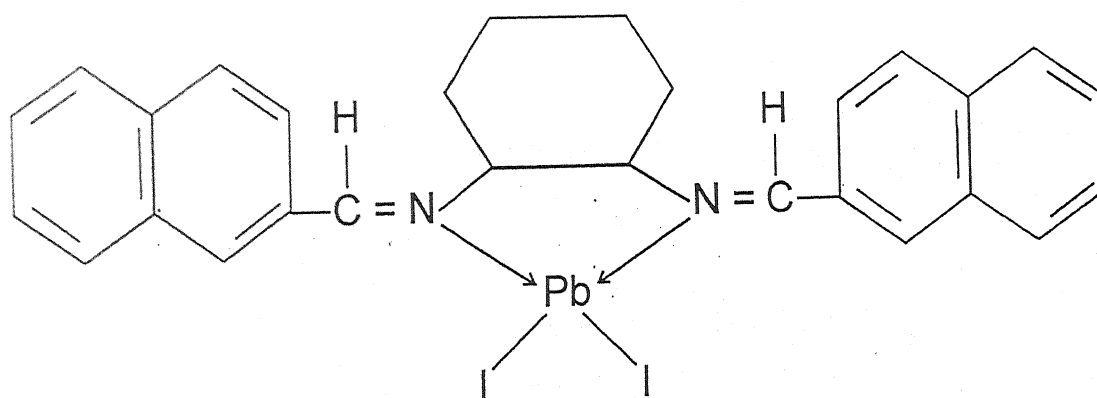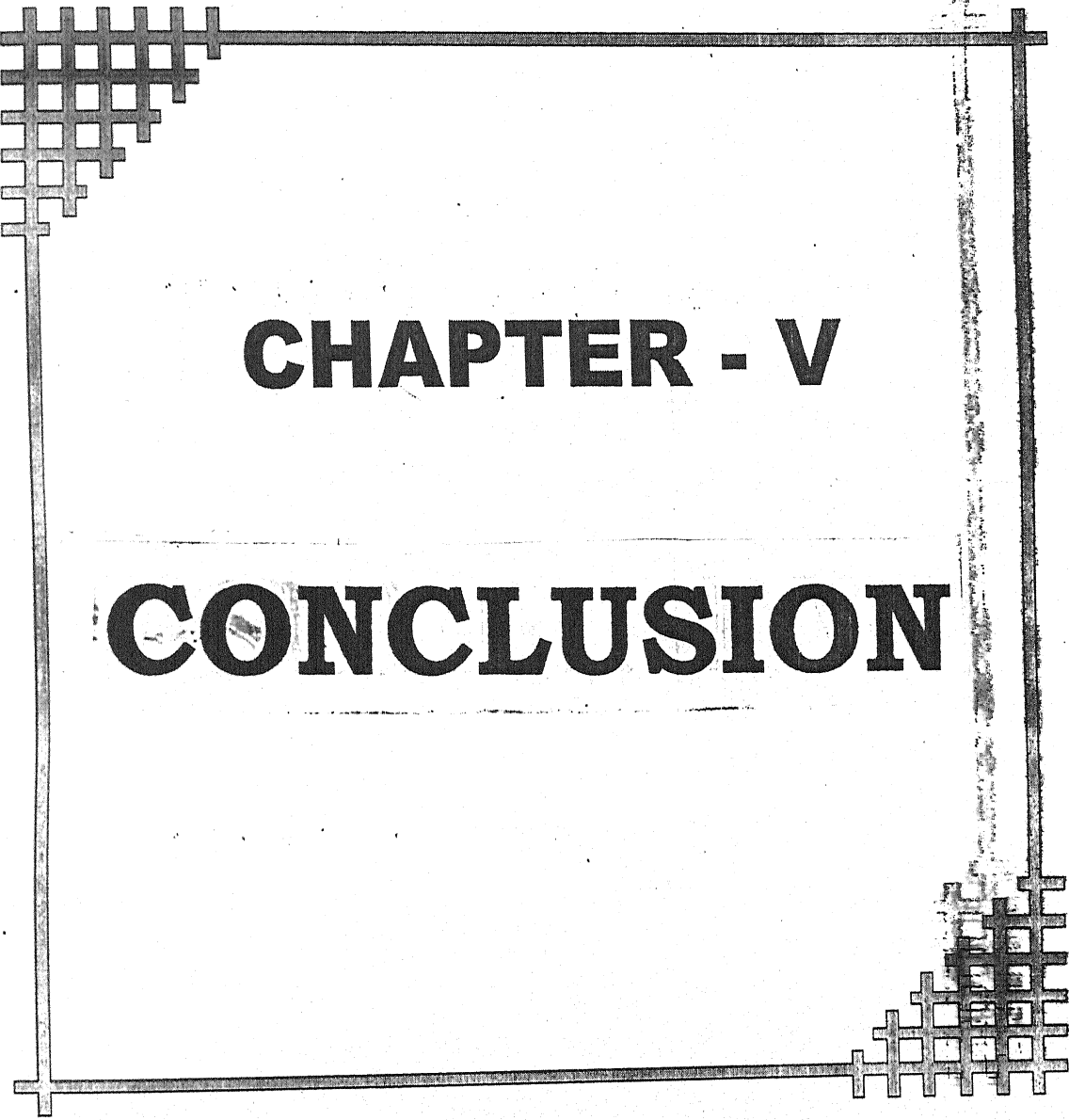
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CHAPTER - V

CONCLUSION

Lead in a ground state configuration has $6s^2 6p^2$ electronic configuration and exists in +2 and +4 oxidation state. It forms covalent lead (II) compounds with the use of unpaired p-electrons e.g. $PbCl_2$. The vacant one 6p orbital can be filled by donor and form compound like $[PbCl_2.D]$ with Sp^3 hybridisation. Moreover, the vacant one 6d- orbital both can be also filled by donors and to form compounds like $[PbCl_2.D]$ with Sp^3d hybridisation.

In the Chapter III, the interaction of $PbCl_2$; $PbBr_2$ and PbI_2 with tetradentate macrocyclic Schiff base ligands i.e. bis (glyoxal) 1,2,4,5 phenylenediamine; bis (2,3- butanedione) 1,2,4,5 phenylenediamine; bis (acetylacetone) 1,2,4,5 phenylenediamine and bis (1-phenylbutane- 1,3- dione) 1,2,4,5 phenylenediamine have been studied in different molar ratio of PbX_2 i.e. 1mmol or 2mmol or 3mmol or 4 mmol and $[PbX_2.D]$; $[(PbX_2)_2.D]$; $[(PbX_2)_3.D]$ and $[(PbX_2)_4.D]$ molecular adducts have been synthesised. These were further characterised by elemental analysis, molar conductance, IR and XPs date to establish structure, which have established their structure as shown in fig. 8-55 in chapter III with sp^3 hybridisation.
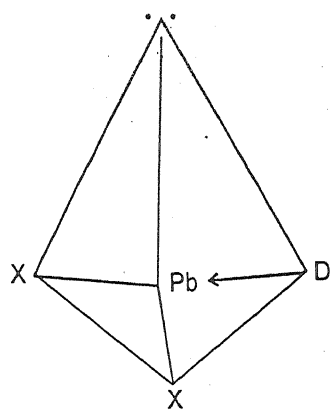
structure of [(PbX$_2$)x.D]

In chapter IV, the interaction of PbCl$_2$, PbBr$_2$ and PbI$_2$ with four bidentate Schiff base ligands i.e. bis (2-acetylepyrrole) cyclohexanediamine; bis (2-pyrrolecorboxy aldehyde) cyclohexanediamine; bis (2-pyridyl carboxy aldehyde) cyclohexanediamine and bis (2-naphthyladehyde) cyclohexanediamine in 1mmol : 1mmol (M : L) have been studied and [PbX$_2$.D] type of molecular adducts are synthesised. All these were further characterised by elemental analysis, molar conductance, IR and XPS data to establish structure; which have established their structure as shown in figs.5-16 in chapter IV with sp^{3}d hybridisation.
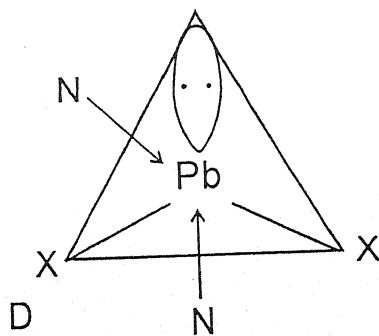
structure of [Pbx$_2$.D] complexes

Since several Schiff base metal complexes have been used as lubricating oil additives[1], in synthetic fiber[2], in dying polyster[3], in photography[4], in synthetic resin industry[5], as corrosion inhibitors[6], as anticancer[7], as antitubmour[8], as antituberculosis agent[9] and as bactericides and fungicides[10], the prepared all PbX_2 complexes of this present work may also immense practical importance.

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